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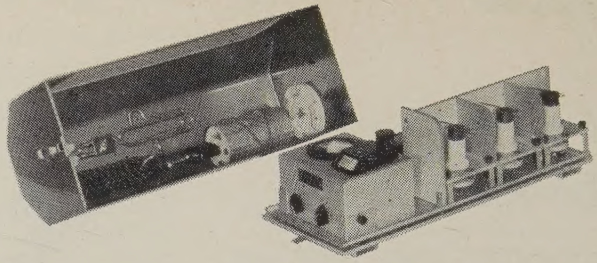

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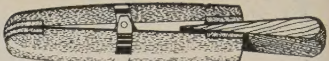

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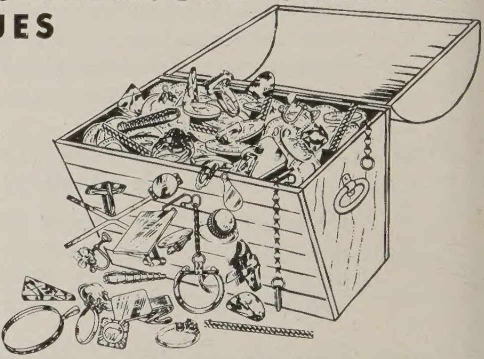

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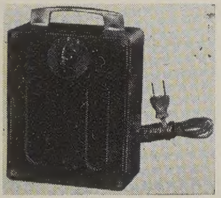

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EXCESS HELIUM AND ARGON IN BERYL AND OTHER MINERALS*

PAUL E. DAMON† AND J. LAURENCE KULP, *Lamont Geological Observatory (Columbia University), Palisades, New York.*

ABSTRACT

All beryl crystals appear to contain a quantity of helium and argon in great excess over that which can be accounted for from radioactive decay. Other magmatic minerals which have structural sites suitable for large non-essential atoms such as cordierite and tourmaline also show this excess in variable amount. It seems that this excess inert gas must represent a sample of the magmatic gases in the immediate environment of the forming crystal and as such can provide useful information on magmatic conditions. Although there are considerable differences in the helium and argon concentration even in the same beryl crystal, these are small compared to the one hundred-fold difference between crystals formed in the early Precambrian ($\sim$3.0 b.y.) and Paleozoic eras. This strong age effect is interpreted as suggesting more extensive outgassing of the mantle in the earlier phases of earth history.

INTRODUCTION

In 1908 Lord Rayleigh (Strutt, 1908) discovered that beryl contained helium in excess of the amount thought to be produced by the decay of the uranium and thorium in the mineral subsequent to its formation. This was in marked contrast to radioactive minerals, sulphides, selenides, arsenides, various native elements, igneous rocks, silica, silicates, phosphates, etc., which usually appeared to be more or less deficient in helium content. Various investigators have confirmed the existence of such an excess for beryl in all samples analyzed (Piutti (1913); Burkser et al. (1937); Hahn (1934); Fay et al. (1938); Khlopin (1941); Aldrich and Nier (1948).) On this point there is no disagreement. Rayleigh (Strutt, 1908) also reported an excess of helium in sylvite, halite and carnallite. Several German and Austrian workers (Hahn and Born (1935); Karlik and Knopf-Duschek (1950)) have also observed this phenomenon and have proposed that an excess of helium in these salts is a result of the decay of co-precipitated short-lived radioactive isotopes such as radium

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* Lamont Geological Observatory Contribution No. 271.

† Present address, University of Arizona, Tucson, Arizona.

and its daughters. A significant excess of helium has also been reported, in a few cases, for magnetite and calcite (Keevil (1941); Hurley (1954)) and for tourmaline and possibly chrysoberyl (Khlopin and Abidov, 1941).

A new dimension was added to the excess helium problem by the isotopic study of He^3 and He^4 by Aldrich and Nier (1948) who obtained He^3/He^4 ratios of 12.0×10^{-7} for atmospheric helium; 0.5–3.0×10^{-7} for twelve natural gas wells; 0.6 to 12.0×10^{-7} for seven beryl crystals; less than 0.3×10^{-7} for five radioactive minerals; and 24.0×10^{-7} and 120×10^{-7} for two spodumene crystals. The abnormal He^3 content of spodumene can be ascribed to the reaction $Li^6(n, He^4)H^3 \rightarrow He^3$ which is the most prolific lithospheric source of He^3 (Morrison and Pine, 1955). It should be noted, however, that equal quantities of He^3 and He^4 are produced in this reaction and so the very large excess of He^4 in beryl cannot be explained by this reaction.

All attempts to explain the origin of the excess helium as a result of nuclear reactions have failed (Morrison and Pine, 1955). This is not surprising in view of another observation by Aldrich and Nier (1948), who found an excess of argon as well as helium in several of the beryls that they studied. The fact that they did not find argon in all of their beryl measurements can probably be attributed to air leakage or the presence of hydrogen in their gas samples. In this work it was found that beryls from the Keystone area (in which Aldrich and Nier found no argon after making a large correction for contaminating atmospheric A^{40}) all have an excess of argon and in fact all beryls studied during this investigation clearly contained a great excess of argon as well as helium.

With the exception of beryl the actual magnitude of the excess gas reported in other minerals is not great. The technical difficulties in both the alpha ($<0.1\alpha$/mg. hr) and helium (volumetric) measurements on these minerals are sufficiently great by older methods that the results should be considered as only tentative.

In the present investigation in which isotope dilution techniques were used, it has been possible to confirm an excess of helium and argon in tourmaline although it is not as great as for beryl in the same pegmatite. In addition it was observed that cordierite also contains an excess of both helium and argon approximately equal in magnitude to that of beryl. A preliminary study of magnetite and calcite, from the localities for which the greatest helium excess was reported, has failed to confirm the actual existence of an excess of argon or helium in these minerals. On the other hand, definite evidence was found for excess inert gas in hornblende from several localities. It is quite possible that the reported excess helium in magnetite is actually due to amphibole contamination. For example, the anomalous samples reported by Hurley and Goodman

(1943) from the Sudbury region actually contained less than 50% magnetite. No evidence has been found for excess argon in mica (Damon and Kulp, 1957*a*).

This paper will be concerned almost entirely with the beryl-like minerals, in which the phenomenon of excess inert gas is most evident and unequivocal. Special attention will be given to the relative and absolute concentrations of these elements and their variation with time.

EXPERIMENTAL TECHNIQUES

The present study required the measurement of the helium content, argon content, potassium content and alpha activity of minerals of known geologic age. In addition the composition of the volatiles contained in several of these minerals was also determined by standard analytical mass spectrometric technique.

The vacuum fusion technique described by Carr and Kulp (1957) for argon and Damon and Kulp (1957*b*) for helium was used for gas liberation and purification. The mineral is fused by induction heating in a molybdenum crucible, mixed with He^3 and A^{38} tracers of known composition in the furnace, and quantitatively removed from the furnace system by the mercury diffusion pump to the purification system where it is purified, equilibrated and eventually sealed off into the sample break seal ampoule. The tracer preparation and calibration system and the mass spectrometric technique have been described in the above mentioned papers. In addition to the determination of He^4 and A^{40}; A^{36}, Ne^{20} and H_2^1 were also monitored during each mass spectrometric determination. In those cases where it was desired to determine the isotopic composition of the inert gases, no tracers were added.

The potassium content of the beryl, tourmaline, and cordierite samples was determined by a simple and inexpensive counting technique. This technique is a modification of the analytical method first described by Gaudin and Pannell (1948). It involves alpha and beta counting of a powdered sample. The beta count is taken with a 5 mil. aluminum absorber to eliminate Rb^{87} betas; this count is then reduced by an empirical correction for the betas resulting from the uranium and thorium series. The alpha count determines the magnitude of this correction. The resulting beta count rate is compared with a standard sample of potassium dichromate to determine the potassium content. Potassium dichromate was chosen as a standard because its density (2.69) is about the same as the silicates in question and also because it is not deliquescent. A Volchok-Kulp (1955) low-level beta counter was used for the work.

The results of a comparison of the α-β method with other methods are given in Table 1.

The precision decreases as the K content decreases due to background fluctuations, but there is no systematic difference. In most cases it was only necessary to set an upper limit on the K content of beryl and cordierite for the excess helium and argon study. Actually the precision of the α-β method does not compare unfavorably with the precision of potassium analyses for silicates in general (Fairbairn et al. 1951).

Alpha scintillation counters of the type described by Kulp, Holland and Volchok (1952) were used. One counter utilized a Dumont 6292 flat faced 2-inch diameter tube with Dupont No. 1101 phosphor. The second counter utilized a 5-inch diameter Dumont 6364 photomultiplier.

Table 1. Comparison of K Analyses by Counting and Other Methods

Sample description	Counting method % K	Comparison method % K
Columbia River basalt (N.B.S. radium std. No. 788)	0.88	0.82
Chelmsford granite (N.B.S. radium std. No. 789)	4.47	3.81
Graniteville granite (N.B.S. radium std. No. 791)	4.30	4.60
Lake Kivu leucitite (GB8)	4.83	5.20 (i.d.)
Hawaiian olivine basalt (SD-2)	0.24	0.35 (i.d.)
Stillwater plagioclase	0.17	0.12 (i.d.)
McKinney feldspar	11.7	11.0 (G)
Wind River Canyon feldspar	9.65	9.39 (G)
Wilburforce antiperthite	3.39	3.73 (L)
Brown Derby feldspar	11.1	10.4 (L)
Black Hills feldspar	11.8	11.8 (L)
Beryl Mt., N.H. albite	0.35	0.39 (L), 0.42 (G)

i.d. = isotope dilution analysis by P. W. Gast.

G = analyzed in the University of Minnesota Rock Analysis Laboratory by the L. Lawrence Smith fusion method (Goldich and Oslund, 1956).

L = determined by Ledoux and Co. using a wet chemical method (Kallman, 1946).

The 2-inch counter was used only for determining the activity of samples for which insufficient material was available to take advantage of the improved geometry of the larger tube. The figure of merit for counting (square of sample count divided by background count) was 8-fold greater for the 6364 than the best obtainable with the 2-inch tube. This allowed low-level samples, which formerly required one week of counting, to be counted with adequate precision during one day.

The alpha counter was monitored by a traffic counter which recorded the accumulated count every 15 minutes. The counters were calibrated with National Bureau of Standards rock samples. Where necessary corrections based upon Bragg's law (Nogami and Hurley, 1948) were made for the composition of the individual sample.

Results and Observations

The experimental data are recorded in Tables 2–6. The detailed sample description may be found in the appendix. Table 2 gives the total A^{40} and He^4 as well as the per cent excess for the samples used in the survey. The geologic ages for most of these samples are well known from Rb/Sr, K/A and/or U/Pb dating in this and other laboratories, but in some cases it was necessary to rely on geological considerations such as the location of a particular sample in the Fennoscandian Shield area etc. (see appendix). Table 3 shows the repeat runs of various kinds. The experimental error in the determination of He^4 and A^{40} content should not exceed a few per cent.* Samples B3, B7, B11 and B13 indicate the

Table 2. Excess Helium and Argon in Beryl, Cordierite and Tourmaline

Sample No.	Locality	Mineral	Estimated geologic age, m.y.	A^{40} in microliters per gm.	He^4 in microliters per gm.	% excess argon	% excess helium
B1	Beartooth, Mont.	Beryl	2,750	32.0	96.2	>99.9	>99.7
B$_2$	Huron Claim, Manitoba	Beryl	2,650	10.0	4.74	n.d.	n.d.
B3*a*, *b*	Greer Lake, Manitoba	Beryl	2,650	~1.5	57	>99.8	>99.8
B4	S. of Greer Lake, Manitoba	Beryl	2,650	~7	102	>99	>99.6
B5	Eräjärvi, Finland	Beryl	1,800	0.74	30.4	>97	>99.7
B6*a*, *b*, *c*	Peerless Mine, Keystone, S.D.	Beryl	1,630	2.2	10.6	>97	>99.7
B7	Keystone, S.D.	Beryl	1,630	1.16	12.9	98	>99.8
B8	Etta Mine, Keystone, S.D.	Beryl	1,630	n.d.	1.22	n.d.	n.d.
B9	Harding Mine, N.M.	Beryl	1,600	0.604	7.12	99	97
B10	Norrbotten, Sweden	Beryl	1,300	0.109	14.2	82	98
B11	Beryl Mt., N.H.	Beryl	320	0.045	0.718	>98	97
B12	Rumney, N.H.	Beryl	320	0.252	3.72	>99.4	87
B14	Haddam, Conn.	Beryl	280	0.152	5.14	99	99
C1	Ft. Victoria, So. Rhodesia	foliated metabasite (cordierite bearing)	2,700	0.613	21.4	>87	>95
C2	Orijärvi, Finland	Cordierite	1,800	0.136	10.6	>96	>99.4
C3	Geelkop, S.A.	Cord. schist	1,100	0.155	4.69	44	90
C4	Kragerö, Norway	Cordierite	1,300	~0.8	1.40	99	83
C5	Rakinankaratra, Madagascar	Cordierite	500	0.171	0.919	>99.3	>99.2
T1	Peerless Mine, Keystone, S.D.	Tourmaline	1,630	0.0182	0.283	60	63
T2	Hugo Mine, Keystone, S.D.	Tourmaline	1,630	0.117	n.d.	95	n.d.

Values preceded by approximation sign (~) were not determined by isotope dilution technique.
n.d. Value not determined.

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* Except in the few cases where only an approximate value was obtained without the aid of the isotope dilution technique.

TABLE 3. VARIATIONS OF HELIUM AND ARGON IN BERYL

Sample No.	Source of beryl	He^4 in micro-liters per gram	A^{40} in micro liters per gram	Remarks
B5	Eräjärvi, Finland		0.735	identical samples
B5	Eräjärvi, Finland		0.748	
B13*a*	Stoneham, Maine		0.220	opposite ends of 6 cm. crystal
B13*b*	Stoneham, Maine		0.165	
B7	Keystone, S.D.	12.9		solid piece of crystal
B7	Keystone, S.D.	10.4		adjacent piece crushed until all material passed through 200 mesh screen
B11*a*	Beryl Mt., N.H.	0.718		aquamarine, 0.22 α/mg./hr.
B11*b*	Beryl Mt., N.H.	0.915		golden beryl, 4.92 α/mg./hr.
B3*a*	Greer Lake, Manitoba	68.0	~2	south pit
B3*b*	Greer Lake, Manitoba	47.0	~1	north pit

location variations which may occur. Sample B11 shows clearly that the excess helium content is definitely not related to the alpha activity. Table 4 shows the results of a search for atmospheric contamination and magmatic neon and A^{38}. Table 5 records the more detailed study of a single large beryl crystal and closely associated tourmaline. Table 6 gives the analysis of the total gases (corrected for blank) derived from three samples of beryl during fusion. The results are reported on a water-free basis as obtained by mass spectrometric technique. Keewatin beryl (Beartooth, Wyoming) and Paleozoic beryl (Beryl Mt., N.H.) contained very nearly the same amount of water (about 0.2%). This was determined by freezing the water into a 300 cc. bulb as evolved during fusion

TABLE 4. He/Ne, A^{40}/A^{36} AND A^{40}/A^{38} RATIOS IN BERYL AND CORDERITE*

Sample No.	Sample location	Mineral	He/Ne	A^{40}/A^{36}	A^{40}/A^{38}
B1	Beartooth, Montana	Beryl	$>4 \times 10^4$	>100,000	≧110,000
B2	Huron Claim, Manitoba	Beryl	$>2 \times 10^5$	>30,000	
B4	S. of Greer Lake, Manitoba	Beryl	$>1.5 \times 10^6$	>48,000	≧65,000
B6	Peerless Mine, S.D.	Beryl	$>4 \times 10^5$	>15,000	
B9	Harding Mine, N.M.	Beryl	$>2 \times 10^4$	>30,000	
C1	Fort Victoria, So. Rhod.	Cordierite bearing foliated metabasite	$>2 \times 10^5$	>18,000	
B5	Eräjärvi, Finland	Beryl	$>6 \times 10^4$	>65,000	≧170,000

* The He/Ne and A^{40}/A^{36} ratios are minimum figures because no correction was made for air leakage. The 38 peak was corrected assuming all of the 36 peak was due to air leakage and so represents the excess over atmospheric. The gas was purified over hot calcium and CuO but there is still the possibility of an impurity and so the A^{40}/A^{38} value is considered to be a minimum value.

TABLE 5. He, A, K CONTENT AND ALPHA ACTIVITY OF A LARGE BERYL CRYSTAL AND TOURMALINE FROM PEERLESS MINE PEGMATITE, KEYSTONE, S.D.

Sample No.	He^4 microliters per gram	A^{40} microliters per gram	K %	Alpha Activity α/mg./hr.	He^4/A^{40}
B6*a*	4.75 (4.63) 4.99	3.97 (3.97)	0.028	0.375	1.2
B6*b*	15.9 (15.9)	3.15 (3.15)	0.011	0.049	5.0
B6*c*	11.1 (10.9)	2.17 (2.11)	0.537*	0.336	5.2
T1	0.283 (0.178)	0.0182 (0.0108)	0.07	0.168	16.5

Numbers in parentheses are the excess Helium and Argon Content.
He^4/A^{40} ratio is for the excess gas.
* Contaminated with sericite.

and then heating the bulb in a warm water bath until the liquid phase disappeared.

These results make possible the following observations:

(1) All beryl, cordierite and tourmaline studied in this work contained

TABLE 6. CHEMICAL COMPOSITION OF THE WATER FREE GASES EVOLVED FROM BERYL DURING FUSION

Constituent	Beryl Mt. beryl B11*a* %	Keystone beryl B7 %	Beartooth beryl B1 %
CO_2	75.0	62.0	75.5
CO	2.5	1.8	2.7
N_2	8.8*	9.7	6.1*
H_2	13.0	20.5	2.0
O_2	0.4	0.1	0.4
H_2	0.07	1.6	9.6
A	0.004	0.2	3.3
CH_4	0.2	3.4	0.3
H_2S	0.02	0.07	0.02
$\frac{N_2+A+He}{CO_2}$	0.12	0.19	0.25
$\frac{A+He}{N_2}$	0.008	0.19	2.1

* Determined by Dr. T. Hoering and Mr. R. Scanlan (Chemistry Department, University of Arkansas).

All other analyses were made by Mr. W. Ault and the authors using a C.E.D. No. 401 mass spectrometer. CO was distinguished from N_2 in the B7 analysis by the relative proportions of m/e=12 and m/e=14.

a large excess of both helium and argon over that required from radioactive decay. In many cases the amount of helium and argon produced within the mineral by radioactive decay was only a fraction of one per cent of the total (Table 2).

(2) The content of helium, argon and potassium and the alpha activity varied in crystals of beryl from the same pegmatite and even within a single crystal (Tables 3 and 5). The content of helium and argon in crystals from different localities is extremely variable. The potassium content of beryl is usually very low ($<0.2\%$). The high value for sample B6C (0.537% K, Table 5) was due to sericite impurity which had not been completely removed. The alpha activity is quite variable ($<.05$ to $5\ \alpha$/mg. hr.) but it is usually less than $1\ \alpha$/mg. hr.

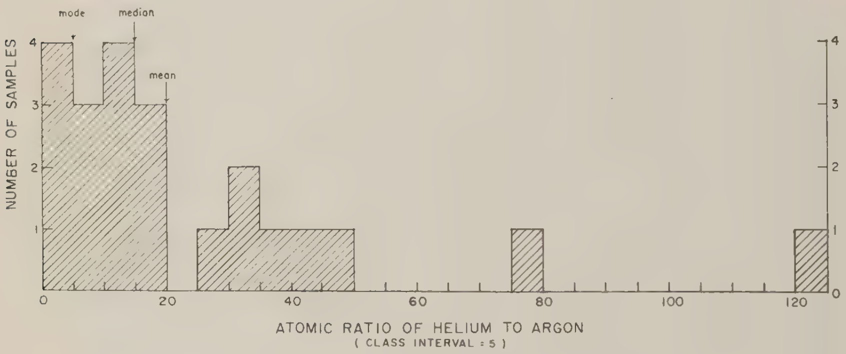

FIG. 1. Ratio of helium to argon in beryl and cordierite.

(3) The ratio of helium to argon in crystals from different pegmatites varied from 0.5 to 130 and even varied from 1 to 5 in a single crystal (Table 5). Qualitatively, it may be stated that the He^4/A^{40} ratio histogram (Fig. 1) is a skewed distribution, with a mode equal approximately to 8, a median value equal to 15 and a mean value of 20. The mode is approximately equal to the relative production rate of helium to argon by radioactive decay in average shale, granite or basalt. The variation of the He^4/A^{40} ratio is much as might be expected from a fortuitous sampling process.

(4) The three minerals for which a gross excess of inert gas has been found have in common an atomic structure based upon a 6-membered silica tetrahedron ring (Bragg (1937); Hambuerger and Buerger (1948)). Beryl and cordierite are isostructural but in cordierite magnesium-aluminum replaces beryllium-aluminum and on the average one aluminum atom replaces one silicon atom in the ring. Fe^{+2} can substitute

partially or wholly for Mg in cordierite. According to Schaller and Stevens (1955), variations in the composition, specific gravity and indexes of refraction of beryl are due to progressive substitution of Li^+ for Al^{3+} along with Al^{3+} for Be^{2+} in the beryl structure; the charge unbalance being satisfied by concomitant substitution of alkali ions, principally Na^+ and Cs^+ into the tubular channels defined by the tetrahedral rings. The structure of tourmaline is much more complex, being composed of alternate layers of 6-membered silica tetrahedra rings with magnesium octahedra and boron triangles, Na^{+1} occupying the central position in the ring.

It can be seen (from Tables 2 and 5) that in the same pegmatite, the magnitude of the excess gas is much less for tourmaline than for beryl. On the other hand, cordierite and beryl appear to accept the inert gases with equal facility.

(5) There appears to be no direct relationship between the helium and argon content and the immediate environment. The beryl crystals occurred in a rather uniform environment of quartz, muscovite and feldspar. The existence of radioactive minerals in a pegmatite (e.g. B2) or the nonexistence of such minerals (e.g. B4) cannot be correlated with the helium content. Cordierite from a metamorphosed terrain such as Orijärvi (C2) or in a metamorphosed basalt (C1) has accepted as much inert gas as beryl of equivalent age (compare C2 with B10) keeping in mind that cordierite composes only a third part of the metabasite (C1 with B3). On the other hand (Fig. 2 and Table 5), the extension of the beryl crystal from the wall zone into the intermediate zone in the Peerless pegmatite was accompanied by a remarkable change in the helium to argon ratio. However, this may be merely a fortuitous correlation.

(6) The elemental and isotopic abundances of the inert gases are not at all similar to their abundances in the atmosphere (Table 4). Neon has not yet been observed in beryl (a more sensitive mass spectrometer is being constructed for this purpose at the Lamont Geological Observatory), but a lower limit can be set on the ratio of helium to neon of at least 10^6 compared with 0.3 in the atmosphere. The ratio of A^{40} to A^{36} is greater than 100,000 to 1 in the Beartooth beryl compared with 295 to 1 in the atmosphere. (The A^{40}/A^{36} ratios given in Table 4 are quite conservative because no effort was made to correct for the small amount of A^{36} which is always present due to air leakage.) The A^{40}/A^{38} ratio is much higher than would be expected from the work of Gerling et al. (1956). These workers found one part of A^{38} per 50,000 parts of A^{40} in mica of Keewatin age after atmospheric correction, and the content decreased in younger micas in such a way as to indicate a potassium parent with a 10^9 year half life. An attempt by J. W. Winchester (1957—private com-

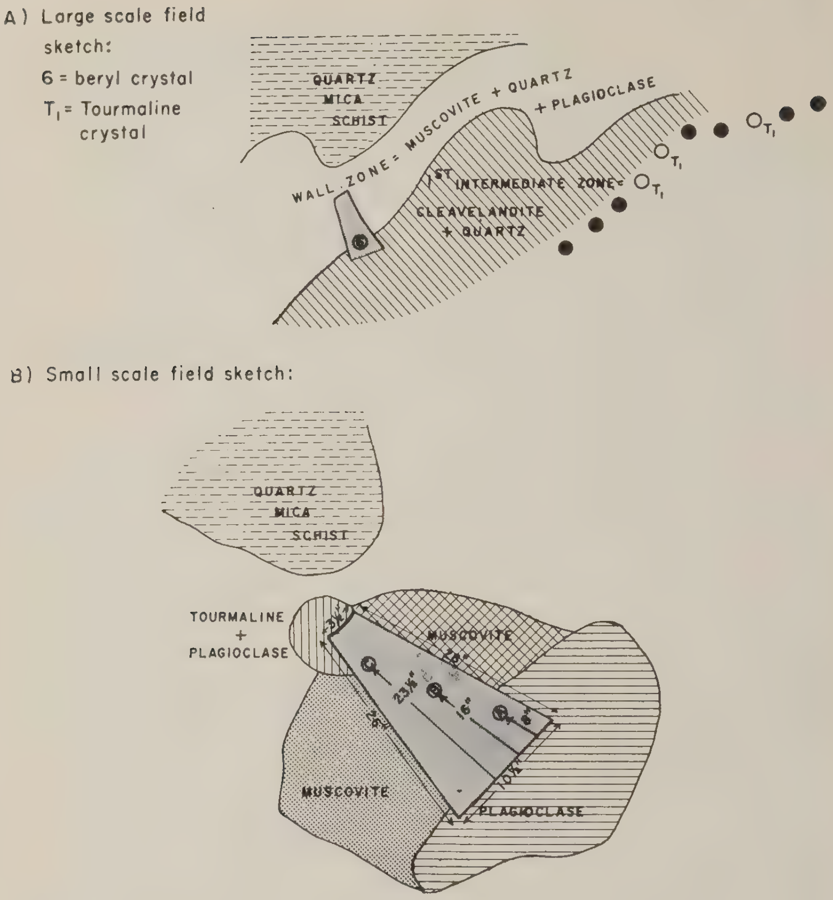

FIG. 2. Peerless Mine pegmatite, Keystone, South Dakota.

munication) to produce long-lived K^{38} by the Ca^{40} (d, α) K^{38} reaction did not succeed.

(7) Lord Rayleigh (1933) analyzed a large number of beryls of different age and came to the conclusion that there was a marked tendency for the oldest beryls to contain the largest quantity of helium. This work has been almost completely overlooked (except for a recent remark by A. Holmes, 1955) in the literature on this subject, despite the ususual quantity of helium ($\sim$.08 std. cc.) observed, for example, in a beryl from a pegmatite south of Yaduir near Bangalore, Mysore, India. The Pb^{207}/Pb^{206} age of monazite from this pegmatite was 2,300 m.y. Khlopin and Abidov (1941), on the other hand, state that there was no connection between helium and mineral age in beryls which they studied.

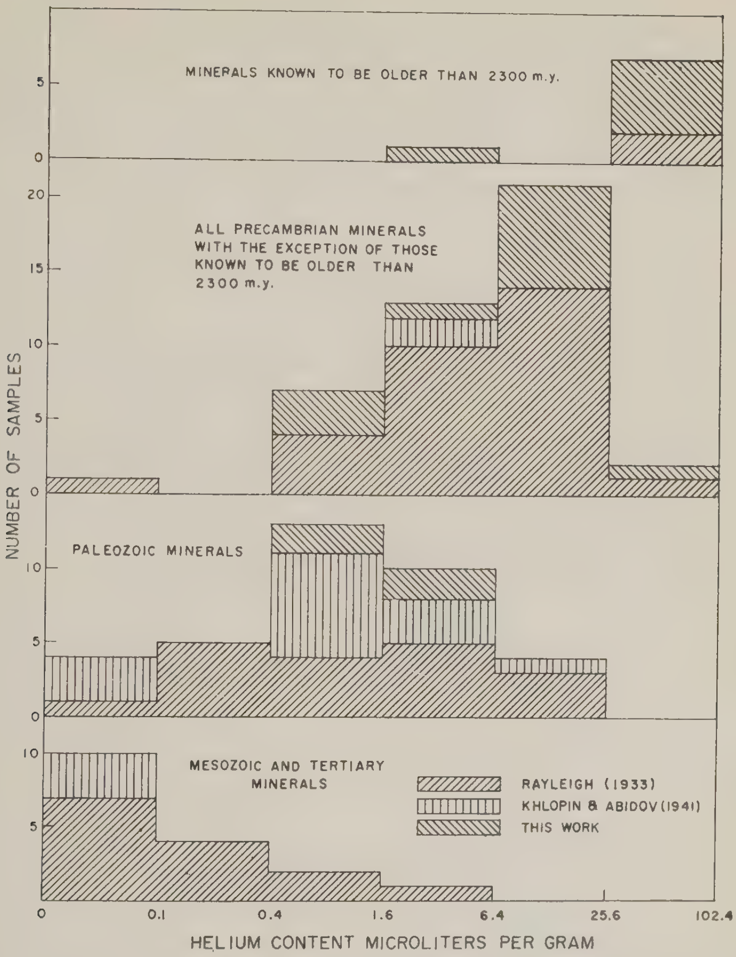

FIG. 3. Helium content of beryl and cordierite of various ages for class intervals arranged according to a geometric progression.

In this work an effort was made to obtain beryl from very old pegmatites in order to decide between the conflicting evidence. The results of the previous investigators have been included with the present work and a histogram has been plotted for the helium content of beryl with the class intervals arranged according to a geometric progression (Fig. 3). A histogram based on exponential (base = 10) class intervals also brings out the relationship but does not distinguish as well between the two Precambrian groups. (Class intervals based on a natural log base would bring out the relationship as well as the geometric progression.) A glance at this histogram confirms Lord Rayleigh's observation and also demonstrates the reason that Khlopin and Abidov did not observe this relationship, i.e., their analyses include only two Precambrian samples.

The relationship is peculiar; qualitatively the helium content increases with age very much as might be expected if beryl were a radioactive mineral containing varying amounts of pure U^{235}, which of course it does not. There is no correlation between alpha emission and helium content. Furthermore, the same age relationship holds for the argon content (Fig. 4). Incidental to this, note that the one beryl from Manitoba which does not fall in the 25.6 to 102.4 microliter per gram class interval contains a quantity of argon second only to the Beartooth beryl from Wyoming. Lord Rayleigh (1933), not knowing about the argon content of beryl, made a fruitless search for an unknown alpha emitter.

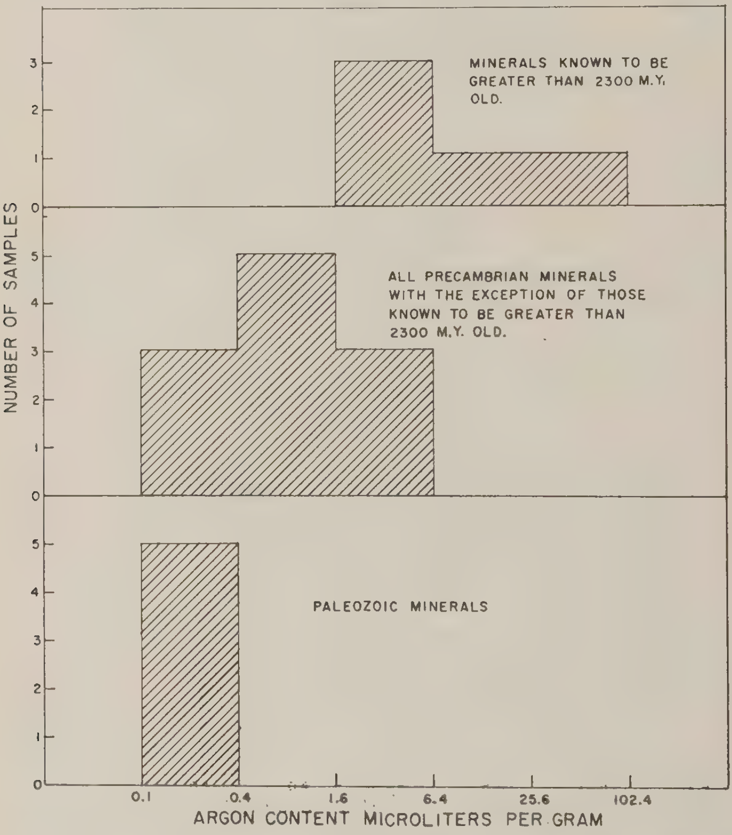

FIG. 4. Argon content of beryl and cordierite of different ages for class intervals arranged according to a geometric progression.

It may be stated that the helium and argon content of beryl and cordierite increases with the age of the mineral and there is no relationship between this phenomenon and the alpha emission, potassium content, chemical composition or mineralogical environment of the mineral.

(8) The chemical composition of gases released from beryl upon fusion is presented in Table 6. The solid pieces of beryl (not powdered) were fused in vacuum without flux and collected without chemical treatment in a 300 cc. bulb. The fusion took place in a molybdenum crucible placed within the quartz-tube furnace. Before melting the beryl the system was carried through a mock fusion without placing a sample in the system. The gases obtained from this "blank run" were, except for the inert gases, very similar in composition to the gases obtained from the

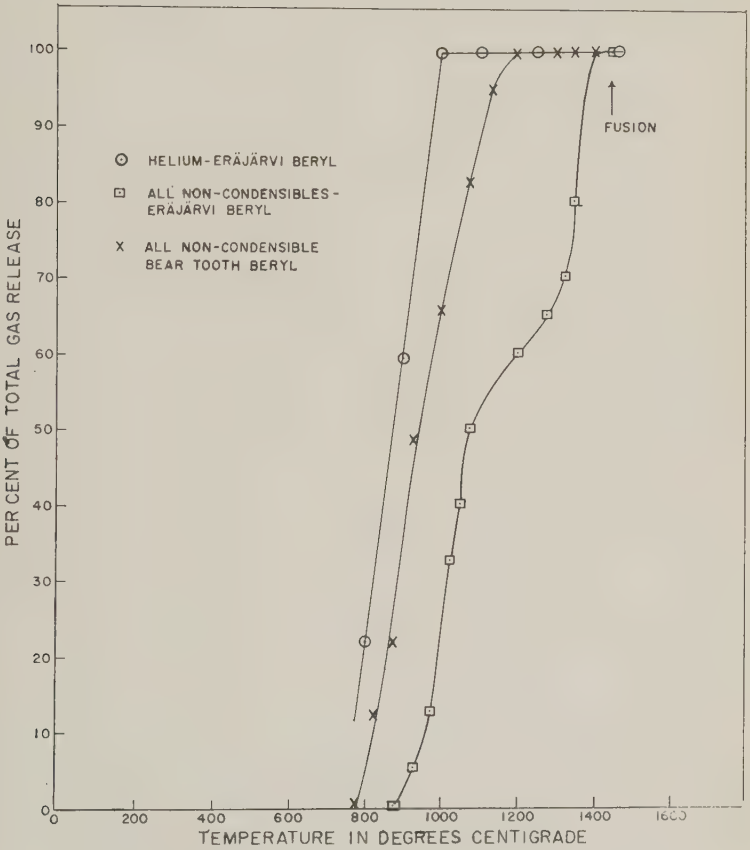

FIG. 5. Release of gas as a function of temperature for beryl.

Paleozoic beryl (B11*a*). Enough beryl was fused to minimize the error due to the blank ($<10\%$ of total volume).

Except for the inert gases and nitrogen the concentrations may not be directly related to primary volatile components trapped in the lattice. Atmospheric gases adsorbed on the surfaces of the beryl undoubtedly contribute to the gases evolved. Furthermore, as pointed out by Wahler (1956), CO, H_2, CH_4, O_2, H_2S can result from decomposition of water, CO_2 and adsorbed organic compounds followed by recombination to produce the observed distribution of the chemical elements among the chemical compounds. As a case in point, through optical prisms it was observed that transport of molybdenum from the crucible to the beryl occurred in the presence of water vapor, presumably by way of an oxide of molybdenum. When beryl was first desiccated by heating to 1200° C. in a graphite crucible, this phenomenon was no longer observed.

Undoubtedly much of the CO_2 and H_2O are more than superficially located within the beryl (the non-essential water content of beryl is well known) and the nitrogen is also most certainly retained within the beryl by more than superficial adsorption. The content of nitrogen and the nitrogen isotope abundances of many of the beryls investigated in this work are being determined by Dr. T. Hoering and associates at the University of Arkansas. Their preliminary results (T. Hoering, personal communication) on a number of beryl and cordierite samples definitely show that the nitrogen content of beryl and cordierite is higher than that of igneous rocks by a factor of 10 to 100.

Thus H_2O, CO_2, N_2 and the inert gases are the most abundant primary constituents evolved upon fusing beryl. For a Paleozoic beryl the proportions are approximately $H_2O=80\%$, $CO_2=16\%$, $N_2=2\%$, inert gases = trace and for the most ancient beryl $H_2O=77\%$, $CO_2=16\%$, $N_2=2\%$ and inert gases$=3\%$. *Thus, the proportion of the inert gases increases but there is essentially no change in* H_2O, CO_2 *and* N_2 *with increasing age.* This can most clearly be seen by the ratio of $(A+He)$ to N_2 in the last row of Table 6.

Wahler (1956) heated beryl until decrepitation and maintained this temperature for only 5 minutes to avoid chemical reactions. The composition of gases evolved by this method was very similar to that observed in the present study but less in volume by a factor of 3 to 4. However, heating for a short period of time at the temperature at which decrepitation first takes place will not completely degas beryl.

The following experiment was performed: A small sample (1 g.) of beryl was heated to 700° C.; this temperature was maintained while chemically active gases were cleaned up on hot calcium, and argon was adsorbed on charcoal at liquid nitrogen temperature until the pressure, as determined by a McLeod gauge, no longer increased appreciably.

Undoubtedly, if this temperature had been maintained for a sufficient period of time, more helium would have been evolved by diffusion, but the value plotted in Fig. 5 represents all the helium that could be readily evolved at this temperature. The temperature was then raised and the process continued until fusion. No change in pressure was observed from 1100° C. to fusion at 1450° C. or thereafter. Thus all of the helium was evolved long before fusion. However, in other experiments (Fig. 5) by observing the manometer reading as the gases came off before clean-up, it was ascertained that the non-condensable gases are most rapidly evolved upon decrepitation but the temperature had to be raised to 1200° C. or higher to completely outgas the beryl. Böse (1936), upon heating powdered beryl, observed that gas was so suddenly and rapidly released upon decrepitation that the powder was blown about in the furnace. This was not observed with the solid pieces of beryl during this investigation. In the case of fine-grained mica, however, flakes may actually be violently ejected from the crucible at about 800° C. if the temperature is raised too rapidly. Böse found that upon decrepitation (zerfalls), which took place between 700–1200° C. for different beryls, there is a decrease in density amounting to from 0.1% to 0.8%. He also states that inclusion free and alkali free beryls decrepitate at higher temperatures. Böse observed the formation of sublimate rings on cooled quartz tubes upon heating beryl powders to 1200° C. The successive sublimate zones contained different metals such as Fe, Ni, Mn, Na, etc. This observation was checked by heating a 5 g. sample of beryl from Harding Mine, N. M. to 1200° C. in a quartz tube which was plugged with glass wool at the cooled end. The glass wool was then placed in 1/1 nitric acid to dissolve metal ions, evaporated to near dryness; distilled water was added and the solution evaporated down to several milliliters. In this case also the Fe, Mn, Na, Be, Li, etc. spectrographic lines* were observed, but there was little or no change in the emission spectrum of the beryl itself before and after heating. In particular the Na lines before and after were identical. It must be concluded, in this case, that the mass transfer was quite small.

ORIGIN OF THE INERT GASES IN BERYL, CORDIERITE AND TOURMALINE

There are three basic hypotheses which may be proposed to explain the excess inert gases in beryl, cordierite and tourmaline:

(1) Helium and argon are created within the crystal lattice by (*a*) an unknown source of radioactivity or (*b*) nuclear reactions.

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* Emission spectrography was done by Dr. K. K. Turekian, Department of Geology, Yale University.

(2) The concentration of the inert gases in these mineral lattices increases with time by diffusion into the lattices from the surroundings.

(3) The "excess" helium and argon were occluded by the mineral at the time of its formation.

It is concluded that the last hypothesis is the only reasonable one.

Hypothesis (1), the internal creation hypothesis, can be dispensed with immediately. A search for the products of necessary nuclear reactions demonstrates that they can only be on the order of 1 part per 10^5 inert gas atoms present. Furthermore, the possibility of the existence of an unknown radioactive source of both argon and helium cannot be taken seriously in view of the extensive nuclear studies which do not indicate either experimental or theoretical possibilities for any radioactive source of A^{40} other than K^{40}. One of the major results of this work was the demonstration that excess argon invariably accompanies excess helium in these minerals which precludes nuclear generation as indicated.

Thus the hypotheses are reduced to occlusion at the time of mineral formation or subsequent diffusion of these constituents into the lattices.

The "excess" helium and argon content might conceivably be accounted for by the diffusion of the inert gases into the crystal lattice progressively with time (hypothesis 2) but this does not appear probable for several reasons. First, the partial pressure of helium and argon into the intergranular spaces must be so much lower than inside the mineral that a sufficient concentration of the correct sign would not be present. The general loss of argon from perthitic feldspars may be cited in this instance. Second, the average 2.7 billion year old beryl has about a 500 fold greater inert gas content than a 0.1 b.y. old beryl, wherever the ages differ by only a factor of 27. Third, diffusion within the crystal carried on for a sufficiently long period of time to explain the age effect would tend to homogenize the inert gases in the mineral rather than support large observed differences in the inert gas content within a single crystal. The large single beryl crystal from the Peerless mine shows a concentration gradient of helium from the center B towards both ends of the crystal in Fig. 2 (see Table 5), whereas the gradient for argon is from the intermediate zone to the wall zone instead of the uniform distribution which would be expected from diffusion. Further, it would appear in this case from the mineralogical environment, the source of the argon would be by way of the mineral plagioclase and thus diffusion would have to defy a 100-fold difference in argon concentration across the mineral interface. It seems most likely that, if anything, both argon and helium should diffuse out of the minerals. Actually, if Schaller and Stevens (1955) are correct, the channels in beryl are not open, being occupied in part by Na^+ and Cs^+ which would block the channels and impede diffusion in either direction.

Occlusion at the time of mineral formation appears to be the correct explanation (Hypothesis 3). The fact that minerals with the six membered ring structure and large open spaces in their lattices are the most prolific source of excess gas must be more than coincidental. *It seems inescapable that occlusion takes place primarily within the channels defined by the six membered rings.* No doubt some occlusion takes place in liquid-gas inclusions. For example, Wahler (1956) observed the spectral lines of helium and argon from the gases obtained from Madagascar quartz by decrepitation. The quartz in this case contained many inclusions. Thus any mineral containing "holes" of any kind which are enclosed in the mineral structure and large enough to contain helium and argon should be considered as a possible source of excess inert gas. Even the amphiboles may contain "excess" inert gas. The position occupied by (Na, K) in hornblende for example is seldom completely filled by the alkali cations and in the ideal tremolite structure it is completely vacant.

Not only the inert gases are enriched in beryl-like minerals. The enrichment of cesium in specimens like the Eräjärvi beryl which contain very little potassium can be explained by the greater ionic radius of cesium. Cesium is not accepted by the feldspars as readily as rubidium. It is concentrated in the residual liquids and gases and can be enriched relative to both rubidium and potassium (Goldschmidt, 1954, p. 166). Thus it is enriched in beryl where it can aid in the $(Na^+, Cs^+) - (Li^+, Be^{+2})$ substitution. Also, as mentioned before, the nitrogen content of beryl and cordierite is 10 to 100 times that of igneous rocks and furthermore, it is present in the molecular form (N_2) primarily rather than as the ammonium ion (NH_4^+) as in igneous rocks (T. Hoering and R. Scanlan, personal communication, 1957).

Since the channels in the beryl-like structure appear to provide a suitable location for the excess inert gases and other "fugitive" constituents, it is unreasonable to imagine that the mineral can form in a pegmatitic environment replete with gases and volatiles, without occluding at least some of these constituents. However, it is necessary to supply a mechanism to keep the gases in the ring. If the gases are relatively loosely bound by Van der Waal's forces, then it is difficult to see why they are not pumped out in vacuum as was observed for a sample of zeolite. Zeolites are very much like charcoal in their behavior towards gases with the exception that the pores in the structure are of constant diameter and cannot accept gas with molecular weights above 50 (Eitel, 1954). Below molecular weight 50, charcoal and the zeolites are analogous. For example, CO_2 is adsorbed more readily than helium. If beryl were behaving in the same way, then more argon would be adsorbed than helium. But this is not the relationship that is observed for beryl; the helium to argon ratio is much as would be expected from the production rates in a pegmatitic environment, making allowance for the greater variability of the trace element uranium and thorium compared with a major element such as potassium (Fig. 2). Water is held much more tightly in beryl than in the zeolites. Upon heating beryl, little water is given off below 800° C., after which water is released rapidly. Furthermore, it is necessary to heat beryl to much higher temperatures before all water is released. No exchange of lithospheric with atmospheric inert gas appears to take place during the weathering process. The Manitoba beryls, which have been exposed to extensive weathering, did not contain a measurable quantity of neon. Thus the occlusion of gases in beryl-like minerals does not appear to be at all similar to the presorption phenomenon and the gases appear to be held in by some such mechanism as a cationic block (suggested by F. E. Wickman, personal communication, 1955). The fact that helium is completely released before other non-condensable gases during degassing can be explained by the more rapid diffusion of the smaller helium atom past the cationic block.

Diffusion is exponentially dependent upon temperature. The self diffusion coefficient increases with temperature according to the following relationship:

$$D_T = D_o e^{-E/RT}$$

where E is the energy of activation per mole, R is the gas constant and T is the temperature. The helium degassing curve for beryl behaves as if not all locations for helium were identical (Fig. 5). At 800° C. not all of the helium comes out at the same rate. In the laboratory experiment, it was necessary to raise the temperature step-wise until at 1100° C. helium was completely released. This could be explained by the cationic block hypothesis. Imagine one of the channels defined by a $[Si_6O_{18}]$ ring containing cations and helium atoms. A particular helium atom in the process of diffusion encounters a Na^{+1} (radius = 0.97 Å) cation and because its Van der Waal's diameter (2.90 Å) is much greater than the space usually available between the cation and oxygen atoms in the tetrahedra (~1Å), it must wait until a fortuitous combination of thermal vibrations allows it to pass. But not all of the cations have the same ionic radius; it next encounters a Cs^{+1} cation (radius = 1.67 Å) presenting a more formidable barrier, etc. In this way the cationic block explains the different locations, each location having a different activation energy E due to statistical fluctuations and variations in the alkali content of beryl which have previously been observed (R. H. Jahns, 1955, p. 1094).

If the deduction is correct, that helium and argon are occluded at the time of mineral formation, then the source of these gases must be in the volatiles present in the immediate environment at the time of mineral formation. The isotopic constitution of the inert gases is what would be expected by derivation from the mantle or crustal rock (originally sedimentary) already degassed of its juvenile or atmospheric inert gases and enriched in He^4 and A^{40} by radioactive decay.

Consider a pegmatite being formed during the process of regional metamorphism; according to Jahns (1955), pegmatites are essentially restricted to terrains of igneous and metamorphic rocks. The first step is the accumulation of molten material along with a gas phase in a relatively (or momentarily) closed volume. The initial partial pressure of the inert gases in the pegmatite before crystallization begins will, of course, be the same as their partial pressure in the immediate environment. This in turn will have been set by (1) the size of the local crustal volume from which the inert gases have been released (2) the degree of completeness of the release in this volume (3) the quantity introduced from the deeper crust and/or mantle (4) the length of time during which temperatures within the source volume are sufficiently high to allow the escape of inert gases from crystal lattices in which they are produced and (5) the production rate of helium and argon throughout the period of time in which they are accumulated preceding and during their mobilization. It is expected that the higher heat production in the mantle and crust in earlier times would produce higher initial partial pressures of the inert gases in the pegmatites due to all five factors mentioned above and, therefore, account for the age effect.

Local variations in the concentration of the inert gases in individual beryl minerals or even within a single crystal are probably a result of continual variation in the partial pressure of these gases during the crystallization of a pegmatite. Several processes are involved here: the rate of crystallization, the relative "tightness" of the pegmatite volume, the hydrostatic pressure.

In most pegmatites crystallization proceeds from the walls inward, concentrating the volatiles in the remaining space. If the enclosing volume is tightly sealed, the vapor pressure will change continually during crystallization. If the volume can lose gas fairly easily, the pressure of the gas phase will be maintained at the hydrostatic pressure for that volume. The actual pressure probably fluctuates considerably from the hydrostatic as the base level. Thus a beryl or portion thereof would contain more or less helium and argon depending on the total pressure at the time of mineral formation.

The concentration of helium and argon being produced by radioactive decay within the pegmatite volume during crystallization is trivial compared to the quantity acquired by mobilization from a much larger volume of rock in which the inert gases have accumulated for a much longer period of time.

It is evident that the age effect cannot solely be due to the *increased rate of production of helium and argon in the past.* This can be shown as follows:

The helium production, 2.7×10^9 years ago, was approximately two-fold greater for the uranium series and 1.15 fold greater for the thorium series. The A^{40} production was higher than at present by a factor of about 4.4. This only provides a factor of two to four, whereas a factor of 100 to 1000 is needed. But the increased rate of heat production by radioactivity during the early period must be taken into consideration. U^{235} and K^{40} produce about 15% of the present radiogenic heat (Rankama, 1954) but 2.7×10^9 years ago they produced about 50% of the total radiogenic heat. The total heat production would also be higher by a factor of two.

The effect of radioactive heat production would be to increase the geothermal gradient in the crust raising the "normal" temperature at any depth. This in turn would allow for greater leakage of argon and helium out of radioactive minerals by diffusion. The other fugitive constituents being chemically active would lag behind, thus raising the partial pressure of helium and argon in the "free" or mobile volatiles. The locus of the incipient pegmatite can be idealized as a small volume of total mobilization surrounded by zones of lesser mobility until in the outermost zone only the inert constituents are significantly mobile. The mobile fugitive constituents are free to mix at this point before recrystallization has begun, the tendency being to occupy any free volume which is accessible and suitable.

Recently Jacobs and Allen (1956) have considered various models for the thermal history of the earth. Concerning a model for a radioactive earth with an initial central temperature of 4500° C., they state (p. 157), "Near the surface, conditions appear to have been greatly different in the far past from those existing at present in fact, there may even have been remelting of material near the surface (down to about 100 km.) during this first thousand million years or so. If so, this could explain the now fairly well-established fact that the Earth as a whole is about 4½ thousand million years old, whereas no rocks have been found much older than about three thousand million years. (A similar suggestion was made by W. D. Urry, some years ago.) However, this brief temperature rise at the beginning soon ceased and cooling commenced. The rate of cooling was greater in the past than it is now, and this suggests that orogenic activity may have decreased with time, and perhaps have been caused by different processes in the far past."

It is the rate of heat production due to radioactive decay which could produce an exponential effect in the quantity of helium and argon released. Derivation of larger quantities of the inert gases from the mantle in the past than at present may contribute significantly toward the age effect. An early extensive degassing of the mantle would release large quantities of nitrogen, inert gases, water and other volatiles to the atmosphere and ocean. Evidence for such an early deep seated degassing has been given in another paper (Damon and Kulp, 1957). Recently Poldervaart (1955, p. 138) has summarized evidence for the chemical evolution of the earth and has concluded that "Initially degassing may have been more rapid in the primitive earth." About 1.8 billion years of earth history took place before the formation of the 2.7 billion year old beryls and cordierite which are listed in Table 2. During this early expanse of time the ratio of inert gas to nitrogen in the mantle would increase because whereas nitrogen (and the inert gases) would be released to the crust and atmosphere, the inert gases would be continually produced in the mantle by radiogenic decay. Recycling of nitrogen in the crust by sedimentation and granitization would maintain a certain proportion of nitrogen in the crust relative to the atmosphere. Thus 2.7 billion years ago as well as at present there would be two sources of inert gases with different composition of volatiles. The mantle would have a relatively high inert gas to nitrogen ratio, whereas the crust would have a relatively low ratio of inert gases to nitrogen. Thus an early extensive degassing prior to 2.7 billion years ago decreasing exponentially towards the present could supply the necessary mixture of crustal and mantle volatiles needed to explain the age effect. In this case the size of the local crust area involved is not as important as the relative contribution in time due to volatiles from a more deep seated source which rise into the crust and permeate the site of regional metamorphism.

It may therefore be concluded that the age effect showing greater helium and argon content in older beryls can be explained by the greater mobilization of the inert gases in earlier times as a result of the increased heat production both in the mantle and the crust. The local variation in concentration of the inert gases in minerals of the same pegmatite can be related to fluctuation in the partial pressure of these gases during crystallization history.

The Effect of Temperature and Pressure

According to Cherdyntsev and Kozak (1949) the amount of helium in beryls increases with increasing temperature of formation. Yoder and Eugster (1955) in their study of muscovite have shown that the relative amounts of Na and K can be used as a geologic thermometer. H. Holland (Personal communication) has applied this to two of the pegmatites that have been investigated during this research, the Beartooth pegmatite

(2700 m.y.) and the Peerless pegmatite (1650 m.y.). The Na-K ratio of muscovite from the Beartooth beryl indicated a temperature of 460° C., whereas the relationship for the wall zone of the Peerless pegmatite indicates a temperature of 550° C. The Na-K ratios for two additional muscovites were also determined. According to the same criteria one of the Greer Lake, Manitoba pegmatites (B4) was emplaced at 520° C. and the Beryl Mt. pegmatite at 540° C. (see appendix). Thus, for these pegmatites Cherdyntsev and Kozak's observation is not correct. Certainly there is no evidence that pegmatites were formed at progressively increasing temperatures in geologic time and so this hypothesis need not be considered further in this connection.

Lord Rayleigh (1933) not having the information now available, favored a nuclear hypothesis to explain the excess inert gases in beryl. Nevertheless, he did point out that the accidents of uncovering of pegmatites favor the exposure of shallow seated young pegmatites and deep seated Archean pegmatites. Deeper burial would provide higher hydrostatic pressures forcing more of the gases into the beryl structure. But the fact that there is no significant variation in the total volume of the volatile constituents, other than helium and argon, eliminates pressure as a direct cause of the age correlation. A 100-fold difference in burial is impossible and even if attained would result in an increase in all the volatile constituents.

It is possible that the quantity of gas occluded by beryl and cordierite may yield valuable information concerning temperature-pressure conditions during pegmatite formation. However, it will be necessary to synthesize beryl and cordierite in the presence of these gases under controlled laboratory conditions in order to obtain this information.

Concluding Remarks

Minerals such as beryl and cordierite provide a most effective method for sampling the volatiles which are present in the environment during the process of regional metamorphism and pegmatite formation. As might be expected, these volatiles consist primarily of water, carbon dioxide, nitrogen and the inert gases.

The excess helium and argon appear to have been trapped at the time of mineral formation and are related to their partial pressures in the immediate environment. The surprising amount of helium and argon in the oldest minerals was not so readily anticipated. Having examined various possibilities it is concluded that the origin of this age effect must be sought in a more extensive mobilization of the lower crust and mantle in the past with a consequent greater rate of degassing of the inert gases than at present. Additional evidence for this greater degassing in earlier times (based upon the isotopic composition of the inert gases, rates of leakage, and present atmospheric abundances), has been treated in another paper (Damon and Kulp, 1957).

There are other minerals which contain "holes" large enough to accommodate helium and argon atoms. Amphibole has been previously mentioned. The structure of the newly discovered mineral osumilite (Miyashiro, A., 1956) is based on a double hexagonal ring, $(Si, Al)_{12}O_{30}$. Unfortunately not enough of this mineral was available for this study. Milarite (Belov and Tarkhova, 1949) and osumilite are isostructural. According to Belov (1942) the Si_6O_{18} ring is also observed in dioptase.

The minerals beryl and cordierite also provide an excellent source for studying nuclear processes occurring in nature which produce the inert gases as end products. Thus in addition to He^3, it is quite certain that nucleogenic Ne^{21}, A^{36}, A^{38} and fissiogenic krypton and xenon isotopes are present in smaller quantities than were observable during this investigation.

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Mr. P. Kluft, Mr. L. Long, Mr. C. Giffin and Mr. F. Bazan assisted in the performance of laboratory experiments. Mr. G. Daniels assisted in the preparation of samples. Dr. K. Turekian was responsible for emission spectrographic analysis of several beryl samples, and Mr. W. Ault assisted in determining the chemical composition of the gases evolved from beryl during fusion. Dr. P. Gast provided several analyses by isotope dilution of the potassium content of rocks and minerals which helped to monitor the wet chemical and radiochemical potassium analyses.

Mr. D. Becknell was responsible for the illustrations of this manuscript and the typing and preparation were done by Mrs. M. Rippey, Miss Joan Sonderburg and Mrs. Marie Mandel.

APPENDIX

Description of Samples

B1	Beryl-collected by Mr. Rae Harris (PD-56-23); one quarter mile south of Blackstone Lake, Bear Tooth, Mont.; orthoclase-quartz pegmatite about 150 ft. long and 10 ft. thick at the widest part; albite and book muscovite 6″ in diameter also occur in the pegmatite; according to Dr. Heinrich Holland of Princeton University, the Na-K ratio for the muscovite indicates that the temperature of formation was about 450° C. Age=2750 m.y. (Gast and Kulp, 1957).
B2	Collected by Dr. F. D. Eckelmann (DE-39–56); grey-white opaque beryl from Huron claim; in potash feldspar-quartz pegmatite containing thin veins of columbite-tantalite; may be followed for 1000 ft. on strike with the Silverleaf-Bear Claim pegmatite about 25′ wide; age 2600 m.y.; see Eckelmann and Kulp (1957) for discussion. Age=2650 m.y. (Gast and Kulp, 1957).
B3*a*	Collected by Dr. F. D. Eckelmann (DE-130-56); light colored opaque beryl with yellow-pink tint from S.E. corner of Greer Lake in S.E. Manitoba; south pit of potash feldspar-quartz-biotite, uraninite bearing pegmatite. Age=2650 m.y. as above.
B3*b*	Same as (DE-130-56) but from north pit, color is white.
B4	Collected by Dr. F. D. Eckelmann (DE-135–56); located about 3000 ft. S.W. of samples B3 (a and b) and part of same pegmatite swarm, about 1000 ft. south of the center of Greer Lake; beryl forms small, euhedral crystals in an elongate band; greenish in color but color varies within mineral and markedly within area of 10×10 ft. Associated muscovite alkali content is $Na_2O=1.43\%$, $K_2O=9.58\%$, $Rb_2O=1.11\%$, indicated temperature=520° C.
B5	American Museum of Natural History collection (A.M.N.H. 24878); from Eräjärvi, Viitaniemi, Finland; white, translucent, cesium beryl; many thin sericite-muscovite veinlets may be seen in thin section; age from location in fennoscandian shield 1800 m.y.
B6*a*	Collected by Mr. L. Long (LL-11a-56); white beryl from single 2 ft. long crystal (see fig. IV-2); from Peerless Mine, Keystone, S. D. Age from micas dated by Mr. Long etc. is 1630 m.y.
B6*b*	As above (LL-11b-56).
B6*c*	As above (LL-11c-56).
B7	Collected by Dr. S. Schaffel from Keystone, S. D. region, white beryl (SS-D-3).
B8	Collected by Dr. K. Turekian (KT-D-3a); from Etta Mine, Keystone, S. D.; milky white; small amount of sericite-muscovite inclusions in thin section.
B9	Columbia University Collection (CU-D-11), from Harding, N. M., piece of large, massive, white specimen, age 1600 m.y. (Faul, 1954, p. 278).
B10	Collection of Mineralogiska Advelningen Natur Historiska Riksmuseet, Stockholm; from Sorkallen near Ranea, Norbotten, Sweden; massive green specimen from large crystal, age thought to be about 1300 m.y. (Dr. F. E. Wickman, personal communication).
B11*a*	Collected by author (BMD-9), Beryl Mt., N. H. pegmatite; this specimen is an aquamarine; the beryl bearing pegmatite has a core of white and rose quartz flanked by a unit 25 to 50 ft. wide consisting of perthite and quartz with large books of muscovite and large circular diameter crystals of albite. Biotite, black tourmaline and garnet are present near the wall zones; for further description of pegmatite see Cameron et al. (1954). This particular specimen contained a large number of tourmaline inclusions visible in thin section; clear translucent and with very little muscovite. Age=323 m.y. (Damon and Kulp, 1957). Associated mus-

covite alkali content is $Na_2O = 1.66\%$, $K_2O = 10.09\%$, $Rb_2O = 0.21\%$, indicated temperature = 540° C.

B11*b* Same as above (BMD-2D), yellow-brown beryl intimately intergrown with quartz and muscovite. Veinlets of sericite-muscovite observed in thin section; also peculiar mosaic structure in thin section but no bubbles. The radioactivity of this beryl was exceptionally high (4.92α/mg. hr.) leading to the supposition that the mosaic structure was due to metamictization. This crystal when heated to 600° C. in vacuum lost its opaqueness and took on a pleasing blue coloration. All beryl (also amazonite) studied, when heated to 1000° C. in vacuum, became opaque white.

B12 A.M.N.H. collection (No. 23798); aquamarine from Rumney, N. H. region; crystal about 4 cm. long embedded in milky quartz. Probably same age as Beryl Mt. pegmatite.

B13*a,b* Columbia University collection (CU-D-4); from Stoneham, Maine; aquamarine, 6 cm. in length; see Cameron et al. (1954). Probably same age as Beryl Mt. pegmatite.

B14 Columbia University collection (CU-D-1); from Haddam, Conn., Gillette quarry; transparent aquamarine, crystal 6 in. long; Cameron et al. (1954), usual muscovite inclusions in thin section; hand specimen veined with quartz. Age = 280 m.y. (H. Faul, p. 267).

C1 Cordierite collected by members of Geological Survey of So. Rhodesia (GB-18); foliated metabasite composed of about $\frac{1}{3}$ cordierite and $\frac{2}{3}$ anthophyllite with sprinkling of opaque accessory minerals; 39 miles E. by N. of Fort Victoria, Ndanga District, Lat. 19° 58′ S., Long. 31° 25′ E., perhaps Sebakwian in age (2,700+m.y.); thought to be a metamorphosed basalt.

C2 Cordierite A.M.N.H. No. 10404 from Orijärvi, Finland; hand specimen is clear, almost transparent blue-grey; crystals and veins of pyrite visible in chips under low magnification, some muscovite on crystal surfaces; muscovite-sericite inclusions visible in thin section; age 1800 m.y. from position in fennoscandian shield; for geological description of the area see P. Eskola (1914).

C3 Collected by Dr. A. Poldervaart; cordierite schist from Geelkop in the Orange R. Valley; according to Dr. Poldervaart, the schist is the result of high grade metamorphism (600°–650° C.). Estimated age = 1100 m.y.

C4 Cordierite (M-D-3) from Kragero, Norway; translucent blue, free of microscopic impurities; age probably 1300 m.y. (from archaeozoic gneiss) (from A.M.N.H. Collection).

C5 A.M.N.H. (17768) from Rakinankaratra, Madagascar; dark blue, translucent, granular cordierite; altered on surfaces; probably late Precambrian in age.

T1 Tourmaline collected by L. Long (LL-12-56) from Peerless mine, Keystone, South Dakota; black tourmaline associated with cleavelandite from quartz-muscovite zone.

T2 Tourmaline collected by L. Long (LL-30-56) from Hugo Mine, Keystone, S. D.; black tourmaline from quartz, plagioclase, muscovite wall zone.

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CERITE FROM MOUNTAIN PASS, SAN BERNARDINO COUNTY, CALIFORNIA*

Jewell J. Glass, Howard T. Evans, Jr., M. K. Carron, and F. A. Hildebrand, *U. S. Geological Survey, Washington 25, D. C.*

Abstract

Cerite, a silicate of cerium and lanthanum, occurs with bastnaesite in one of the rare-earth-bearing veins of the Mountain Pass district, California. The deposits of rare-earth minerals are in a mineralized zone in shonkinite in an area of Precambrian metamorphic rocks. The minerals associated with cerite are: bastnaesite, barite, quartz, chalcedony, calcite, galena, and altered acmite. Cerite is verona brown and occurs in massive form and in crystals. The crystals are pseudo-octahedral and range in size from 2 to 7 mm. The mineral has a resinous luster, a hardness greater than 5, and no observable cleavage. It gelatinizes in hot acid. The specific gravity as determined on the Berman microbalance is 4.78 ± 0.11. The mineral is uniaxial positive, and the indices of refraction are $\omega = 1.806$ and $\epsilon = 1.808$. X-ray single-crystal studies show that the crystals are rhombohedral rather than orthorhombic as suggested by Nordenskiöld, and have the following characteristics: space group $R\bar{3}c(D_{3d}^6)$ or $R3c(C_{3v}^6)$; hexagonal $a = 10.78 \pm 0.08$ Å, $c = 38.03 \pm 0.27$. Crystal forms present are $c\{0003\}$, $e\{01\bar{1}2\}$. The chemical analysis of purified material, after about 4 per cent of impurities are subtracted, is interpreted in terms of chemical, physical and crystallographic properties to give the tentative formula: $(Ca, Mg)_2(RE)_8[(SiO_4)_{7-x}(FCO_3)_x][(OH)_x(H_2O)_{3-x}]$.

Introduction

The rare mineral cerite, a silicate of cerium and lanthanum, occurs in one of the rare-earth-bearing veins of the Mountain Pass district, San Bernardino County, California. This occurrence is the second known of this mineral in the United States. The first occurrence is near Jamestown in Boulder County, Colorado, and was described by Goddard and Glass (1940). Cerite was first discovered a century and a half ago at Bastnäs, Sweden (Hisinger and Berzelius, 1804, 1806) and the study of this new mineral led to the discovery of the element cerium. Since the discovery of cerite in Sweden at two places, two other minor occurrences have been recorded outside the United States: one in the Kyshtymsk (Kychtym) district in the Ural Mountains, Russia (Silberminz, 1929), and one in Papineau County, Quebec, Canada (Goddard and Glass, 1940). Cerite from Mountain Pass, California, was identified in the course of mineralogic and petrographic examinations of ore samples as a part of the investigation of rare-earth mineral deposits by the U. S. Geological Survey.

The Mountain Pass district, San Bernardino County, California, is traversed by U. S. Highway 91, about 35 miles east of Baker, and 60 miles southwest of Las Vegas, Nevada. The vein containing cerite is known as "Vein No. 6" in the Birthday group of claims, where the original discovery of bastnaesite in the district was made in 1949. The specimens were taken from a prospect cutting the vein 200 ft. due east of the Birthday Vertical Shaft (Olsen, Shawe, Pray and Sharp, 1954, plate 10). Thus far, cerite has been found only in this vein, although it is not improbable that the mineral may be identified elsewhere in the district.

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* Publication authorized by the Director, U. S. Geological Survey.

The specimens were provided by D. F. Hewett, U. S. Geological Survey. R. W. Lewis, Boulder City Station of the U. S. Bureau of Mines, courteously provided *x*-ray data made independently on duplicate specimens. W. T. Pecora, U. S. Geological Survey, contributed data on the geology. Several colleagues generously assisted in establishing the identification of cerite. Spectrographic examinations were made by K. J. Murata, H. J. Rose and E. L. Hufschmidt. J. M. Axelrod assisted in the *x*-ray diffraction studies. Appreciation is expressed also to the U. S. National Museum through whose cooperation specimens from other localities were secured for comparison. Finally, we wish to thank Dr. P. Gay of the University of Cambridge, who kindly gave us helpful information in connection with the crystallographic study.

Geology and Occurrence

The geology of the Mountain Pass district has been described by Sharp and Pray (1952) and by Olson, Shawe, Pray and Sharp (1954). The Mountain Pass district is in the northeastern part of San Bernardino County, about 12 miles from the Nevada state line. The Birthday claims are in the northern part of the district. Vein No. 6 is in the second quadrant from the upper right, S 1375, W 970, at 200 feet due east from the Birthday vertical, two-compartment shaft, map by Sharp and Pray (1952), and plate 10, Olson, Shawe, Pray and Sharp (1954). The region in which Vein No. 6 is found is characterized by Precambrian metamorphic rocks, including granite gneiss and mica schist. The dominant rock in the immediate area of Vein No. 6 is shonkinite, an alkalic rock that has intruded the metamorphic complex. Extensive alteration and replacement took place along fractures to form the quartz-barite-carbonate veins within which rare-earth minerals including cerite and bastnaesite are found.

The mineral assemblage in Vein No. 6 includes cerite, bastnaesite, barite, quartz, chalcedony, calcite, galena, and acmite. Hand specimens and thin sections show bastnaesite and quartz to be younger than cerite. Crystals of bastnaesite are locally perched on cerite in some cavities. In some areas the two minerals are intimately intergrown in indistinguishable relationships; in other areas the cerite and bastnaesite occur in parallel growth (Fig. 1).

A more detailed description of the associated minerals is given below:

Barite—Barite is one of the most abundant minerals in the cerite-bastnaesite-bearing vein. As much as 25 per cent of the vein materials is massive barite. Most of the barite is white, but some of it is stained pink; a little of it is colorless and transparent. Much of the barite has been dissolved, leaving a cavernous skeleton.

Bastnaesite—Bastnaesite, a fluocarbonate of cerium metals, occurs in Colorado at Jamestown in intimate association with the cerite, and at Pikes Peak, Allen and Comstock (1880), and at Bastnäs, Sweden. Geijer (1920, 1921) states for the cerite from Sweden, "There is, in fact, hardly one thin section with any notable percentage of cerite that does not also contain bastnaesite, often making up one-third or more of the cerite ore." In the coarser cerite-bastnaesite vein material from Mountain Pass, the bastnaesite occurs in alternate bands with the cerite (Fig. 1) and in cavities in the barite and quartz. Small tabular crystals of pale-yellow, nearly colorless bastnaesite are found attached to the cerite crystals and commonly also attached to galena crystals. The variation in the types of occurrence and in the bastnaesite itself may be the result of repeated periods of hydrothermal action.

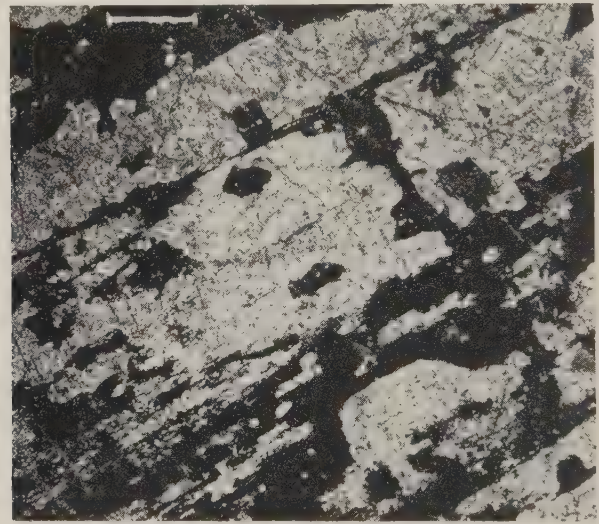

FIG. 1. Photomicrograph of a thin section of a specimen from vein No. 6, Mountain Pass, San Bernardino County, California, showing subparallel intergrowth of cerite (black) and bastnaesite (light gray). Crossed nicols; bar at top indicates 1 mm.

The interstitial bastnaesite has the following optical properties: the optic sign is uniaxial positive, and the indices of refraction are $\omega = 1.721$,

$\epsilon = 1.822$; the pale-yellow, nearly colorless crystals from cavities have the indices, $\omega = 1.718$, and $\epsilon = 1.818$.

Calcite—Glassy clear calcite is found in cavities in the barite and in the quartz. In places it occurs as part of the vein-filling mass.

Chalcedony—Opaline chalcedony was deposited late. It is found on the walls of cavities in the massive quartz, and as a covering over crystals of cerite and bastnaesite.

Galena—Galena crystals and aggregates of small crystals 5 mm. to 1 cm. across are found commonly in cavities loosely attached to the walls and partly replaced by quartz and bastnaesite. Nearly all the galena is covered completely by a crust of drusy bastnaesite, and the crust is shielded by a thin covering of chalcedony. The galena seems to be a relict that survived hydrothermal alteration.

Pyroxene—Extremely altered, high-index pyroxene that shows some of the properties of acmite is found in small patches of grayish-green fibers about 1 cm. long embedded in the quartz-barite areas of the vein material. It, like galena, seems to be a remnant of a preexisting rock.

Quartz Quartz is the most abundant mineral in Vein No. 6. It is dull pinkish gray and finely crystalline. It shows the marks of severe attacks of invading solutions. In some areas the quartz is cavernous and serves as host rock for the other minerals.

The identification of cerite as a vein mineral in the Mountain Pass district adds to the list of rare-earth minerals identified in this district since the discovery of bastnaesite in 1949. Cerite is probably older than most of the bastnaesite in the same vein. Hydrothermal attack and formation of porous quartz and opaline chalcedony characterize the late mineralization in the vein. Cerite is a rare mineral in the district, and, if originally more widespread in distribution, it probably has disappeared by hydrothermal alteration.

Physical and Optical Properties of Cerite

Cerite from Mountain Pass is verona brown (burnt umber) in color. Thin fragments are pale lavender brown to colorless. The mineral occurs massive and in crystals. The crystals have a pronounced pseudo-octahedral habit and vary in size from 2 mm. to 7 mm. across. They occur as clusters in cavities in the massive cerite, or as single crystals in a matrix of barite or calcite (Fig. 2 and Fig. 3). The mineral has an uneven fracture and no observable cleavage, a resinous luster, and a hardness slightly greater than 5. It gelatinizes in hot hydrochloric acid. Repeated

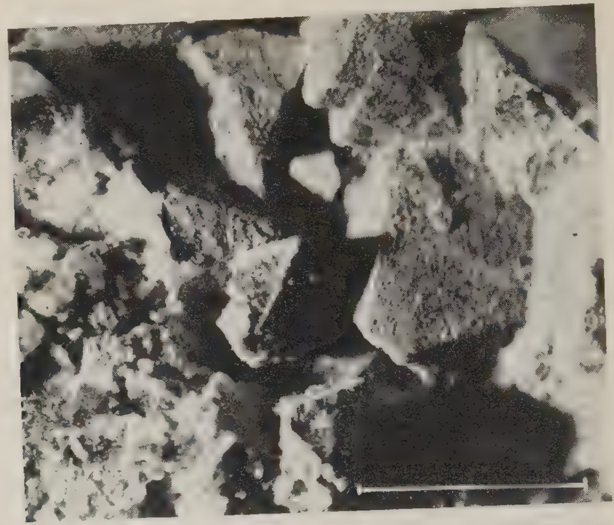

FIG. 2. Crystals of cerite in a cavity of drusy quartz from Mountain Pass, San Bernardino County, California. Direct light; bar indicates 1 cm.

determinations of the specific gravity of 10- to 20 mg. samples with the Berman balance yield an average value of 4.75±0.11. The variation among individual measurements is considerable, and suggests a poor crystalline texture.

Under the microscope, thin sections or thin fragments of the mineral are commonly sensibly isotropic. Thick grains vary from nearly isotropic

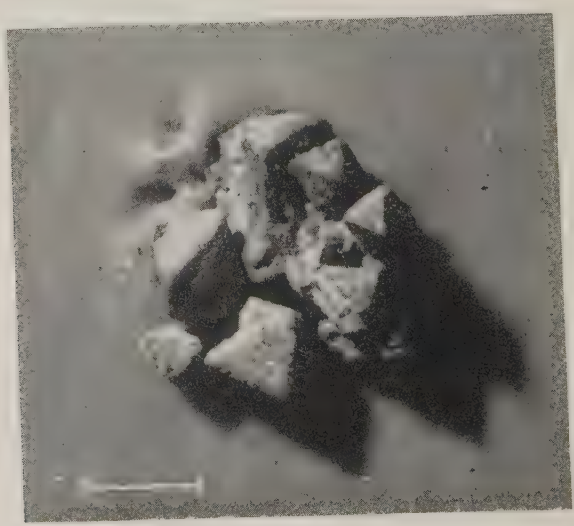

FIG. 3. Cluster of cerite crystals perched on massive cerite from Mountain Pass, San Bernardino County, California. Specimen mounted on wax. Bar indicates 1 cm.

to faintly anistropic with undulatory extinction in the same grain, presumably resulting from internal strains. Under high magnification some grains revealed cloudy areas of included material, possibly bastnaesite, as this mineral is always detected in the *x*-ray powder patterns of cerite. Optical axial figures are seldom observed; they vary from uniaxial to very small 2V, biaxial positive. The indices of refraction are $\omega=1.806$, and $\epsilon=1.808$. Such low indices of refraction for cerite have not heretofore been noted. The optical properties of cerite from different places are compared in Table 1.

TABLE 1. COMPARISON OF OPTICAL PROPERTIES OF CERITE

	California 1	Colorado 2	Sweden 3	Sweden 4	Urals 5
α (ω)	1.806	1.815	—	1.817	1.810
β	—	1.815	1.81	1.818	—
γ (ϵ)	1.808	1.820	—	1.821	1.825
Birefringence	0.00–0.002	0.005	0.002	0.004	0.015
Sign	+	+	+	+	+
2V	0° to very small	0° to 8°	0° to small	25°	11°

1. This investigation.
2. Goddard and Glass (1940).
3. Geijer (1920, 1921).
4. Larsen and Berman (1934).
5. Silberminz (1929).

CRYSTALLOGRAPHY OF CERITE

Crystal fragments of cerite from Mountain Pass, California, were studied by the Buerger precession method. The crystals are rhombohedral, with the following crystallographic elements:

Space group: $R\bar{3}c$ (D_{3d}^6) or $R3c$ (C_{3v}^6)

Cell dimensions:

$$\left.\begin{aligned} a &= 10.78 \pm 0.08 \text{ Å} \\ c &= 38.03 \pm 0.27 \end{aligned}\right\}\text{hexagonal}$$

$$\left.\begin{aligned} a_R &= 14.12 \pm 0.11 \text{ Å} \\ \alpha &= 45°07' \pm 57' \end{aligned}\right\}\text{rhombohedral}$$

Cell volume: 1280 ± 16 Å^3 (rhombohedral)

Morphological elements: $a:c=1:3.527$

$p_0=4.072$

Forms: $c\{0003\}$, $e\{01\bar{1}2\}$

The crystals are crudely formed, but the forms listed above can be identified. The forms are about equally developed, giving the crystals a pronounced pseudo-octahedral aspect, as shown in Fig. 4 ($c \wedge e=66°17'$;

$e \wedge e = 80°0'$). The crystals appear holohedral in habit and give no positive piezoelectric response in the Giebe-Sheibe apparatus; therefore, the structure is probably centrosymmetric.

On the single crystal photographs, those reflections with l odd are absent for the $(h0.l)$ reflections, owing to the glide plane; but in addition, for the $(hk.l)$ reflections, they are relatively weak and occur at large Bragg angles. Thus, the structure has a rhombohedral pseudocell, with $c = 19.08$ Å, one-half the true c axis length. The rhombohedral pseudolattice is in the negative mode with respect to the true lattice so that in this setting, the crystal form $e\{01\bar{1}2\}$ becomes the unit positive rhombohedron $\{1011\}$.

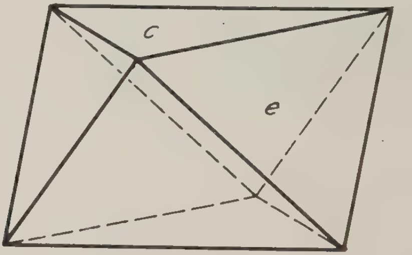

FIG. 4. Crystal habit of cerite from Mountain Pass, San Bernardino County, California. Crystal forms: $c\{0003\}$, $e\{01\bar{1}2\}$.

The powder diffraction pattern of Table 2 has been indexed on the basis of the true cell, but calculated spacings for reflections with l even only are listed. The powder pattern shows no clear evidence of metamict properties, and the pattern is virtually unchanged for a sample heated to 900° C.

In a recent short article by us (Glass, Evans, Carron and Rose, 1956), the Mountain Pass cerite was described as monoclinic. Following a kind personal communication from P. Gay of Cambridge, England, who has made a new study of cerite from Bastnäs (Gay, 1957*b*), the higher rhombohedral symmetry for the California material was found in the single crystal photographs (Gay, 1957*a*). The primitive unit cell of the rhombohedral lattice defined here and the body-centered monoclinic lattice assumed earlier have equivalent dimensions and the same volume. Gay (1957*a*) has pointed out that there is a possibility that the hexagonal lattice is primitive rather than rhombohedrally centered, but no trace of any reflections that would support such a hypothesis has been found on the many precession photographs made of the Mountain Pass crystals.

The single crystal diffraction patterns were made from euhedral fragments about 1 mm. in cross section. Because of the moderate distortion of the texture of the crystal, smaller fragments did not give any im-

TABLE 2. POWDER-DIFFRACTION DATA FOR CERITE

Calculated spacings based on rhombohedral cell, space group $R\bar{3}c$ (or $R3c$); hexagonal $a=10.78$, $c=36.03$ Å, $l=2n$ only.

Measured spacings based on F. A. Hildebrand film no. 8689, FeKα radiation, 114.7 mm. diameter camera, cutoff 17.0 Å.

hk.l	*d* (calc)	*d* (obs)	*I*	*hk.l*	*d* (calc)	*d* (obs)	*I*
01.2	8.39	8.40	13	40.10	1.990		
10.4	6.66	6.67	7	21.16	1.972		
00.6	6.34	6.35	6	11.18	1.967		
11.0	5.39	5.40	9	23.8	1.954	1.954	50
20.2	4.53	4.53	17	41.6	1.947	1.939	13
01.8	4.24	4.23	12	31.14	1.870		
02.4	4.19			32.10	1.867		
11.6	4.10			50.2	1.865		
10.10	3.523	3.51	15	01.20	1.864	1.863	25
12.2	3.472	3.47	42	05.4	1.839	1.834	12
20.8	3.332			33.0	1.798	1.799	15
21.4	3.310	3.31	33			1.791	5
00.12	3.170	3.17	7	20.20	1.766		
30.0	3.113	3.11	30	13.16	1.752		
02.10	2.949	2.95	100	30.18	1.748	1.748	25
12.8	2.835	2.83	38	24.4	1.741		
30.6	2.795	2.80	27	50.8	1.739	1.740	9
11.12	2.733			33.6	1.729		
22.0	2.696	2.69	42	14.12	1.720	1.717	5
01.14	2.596			10.22	1.700		
21.10	2.587	2.59	21	05.10	1.683		
31.2	2.567	2.57	7	23.14	1.679	1.679	10
13.4	2.500	2.50	5	15.2	1.677		
22.6	2.482	2.44	3	12.20	1.674		
20.14	2.349			40.16	1.666		
04.2	2.318	2.31	7	22.18	1.663		
10.16	2.304			42.8	1.655	1.655	7
31.8	2.275	2.27	7	02.22	1.622		
40.4	2.267			32.16	1.592	1.593	13
30.12	2.222	2.22	25	15.8	1.587		
12.14	2.146			00.24	1.585	1.583	8
13.10	2.141	2.14	9	21.22	1.553	1.566	9
23.2	2.130			50.14	1.537	1.535	8
02.16	2.119	2.13	7			1.515	6
00.18	2.113					1.496	8
04.8	2.096	2.09	12			1.456	7
32.4	2.090	2.07	5			1.424	12
41.0	2.045	2.04	9				

provement in the somewhat crude appearance of the patterns. The precession patterns showed several powder rings in addition to the spot patterns of cerite. The ring pattern, which is characterized in Table 3,

TABLE 3. POWDER-DIFFRACTION RINGS ON CERITE PRECESSION PATTERNS
Indexed for bastnaesite with $a=7.14$, $c=9.78$ Å

Line no.	I	d (obs)	d (calc.)	hk.l
1	SO	4.94 Å	4.89 Å	00.2
2	W	3.57	3.57	11.0
3	WM	2.88	2.88	11.2
4	MO	2.44	2.44	00.4
5	W	2.05	2.06	30.0

S = strong, M = medium, W = weak, O = oriented.

has been identified with bastnaesite. In order to confirm the identification, a powder diffraction pattern of bastnaesite from Mountain Pass has been measured and indexed as shown in Table 4. (Because of the special positions which the heavy scatterers -the cerium atoms—have in the bastnaesite structure, powder lines for the class of reflections for which $(h-k)=3n$ and $l=2n$ only are to be expected, except for a few weak lines at low Bragg angles.) Two of the bastnaesite powder rings which appear on the cerite single crystal patterns, namely (00.2) and (00.4), are strongly concentrated in certain directions. This preferred orientation effect is such as to indicate that the bastnaesite is the light-colored coating visible on the surface of the cerite crystals, and is strongly oriented with the hexagonal *c* axis tending to lie normal to the crystal surfaces.

Nordenskiöld (1873) has described the morphology of crystals of cerite from Bastnäs, Sweden, and the System of Mineralogy (Dana, 1896) follows this description. The habit and crystallography (orthorhombic) of Nordenskiöld's crystals bear no resemblance whatever to that found for Mountain Pass crystals. On the other hand, the *x*-ray powder patterns obtained for cerite from Mountain Pass, Jamestown, and Bastnäs are all identical (if the varying admixture of bastnaesite is taken into consideration). Professor Clifford Frondel of Harvard University very kindly loaned us a specimen of the type material from Bastnäs, which was presented to the Harvard museum by Berzelius in 1807. A powder pattern of cerite from this specimen again proved to be identical to that of the Mountain Pass cerite, with a fairly strong bastnaesite pattern superposed. In light of the accumulated evidence, the identity of cerite cannot be doubted. Nordenskiöld's crystallographic measurements cannot be reconciled with ours.

CHEMISTRY OF CERITE

Observations made on specimens from all the known deposits of cerite show that the mineral habitually occurs with some other cerium earth

TABLE 4.—POWDER-DIFFRACTION DATA FOR BASTNAESITE, BIRTHDAY CLAIM, MOUNTAIN PASS, CALIF.

Hildebrand film No. 5888, Hexagonal, $P\bar{6}2c$, $a=7.129$ $c=9.774$ Å; CuKα radiation, d cutoff at 12.0 Å.

$hk\cdot l$	d (calc.)	d(obs.)	I	$hk\cdot l$	d (calc.)	d (obs.)	I
00.2	4.887	4.881	42	22.8	1.0087	1.006	6
11.0	3.564	3.564	71	60.2	1.0073		
11.2	2.880	2.879	100	52.0	.9886	.988	3
20.2*	2.609	2.610	1	00.10	.9774		
00.4	2.445	2.445	9	52.2	.9689	.9689	7
10.4*	2.272	2.273	3	33.6	.9599	.9585	2
20.3*	2.241	2.238	3	60.4	.9482	.9480	3
30.0	2.058	2.057	42	11.10	.9427	.9425	3
11.4	2.016	2.016	42	52.4	.9164	.9162	5
30.2	1.898	1.898	42	41.8	.9050	.9048	5
22.0	1.782	1.783	9	44.0	.8911	.8908	2
22.2	1.674	1.674	21	30.10	.8829	.8827	2
00.6	1.629	1.629	1	44.2	.8766	.8766	3
30.4	1.574	1.573	15	60.6	.8699	.8701	3
11.6	1.482	1.481	9	22.10	.8569	.8569	3
22.4	1.440	1.439	11	33.8	.8518	.8520	3
41.0	1.347	1.347	7	52.6	.8451	.8451	5
41.2	1.299	1.298	15	44.4	.8372	.8369	3
30.6	1.277	1.277	7	71.0	.8176	.8175	3
00.8	1.222	1.223	2	00.12	.8145	.8070	6
22.6	1.203	1.204	6	11.12	.7921	.7920	4
33.0	1.189	1.190	3	41.10	.7892	.7892	6
41.4	1.180	1.180	9	60.8	.7851	.7851	3
11.8	1.156	1.156	11	44.6	.7799	.7799	4
33.2	1.155			63.0	.7760	.7760	5
33.4	1.069	1.068	4	71.4	.7737	.7737	7
30.8	1.051	1.050	4				
41.6	1.038	1.038	6				
60.0	1.029	1.028	2				

Note: All Reflections for which $l=2n$ and $(h-k)=3m$ are calculated, plus those marked (*). d(obs.) corrected for film shrinkage of 0.216%.

mineral. At Mountain Pass, bastnaesite is the principal contaminant, from which it is very difficult to separate the cerite.

To prepare cerite for chemical analysis, a sample that weighed 103 grams was selected from a part of Vein No. 6 that showed the greatest concentration of cerite. The sample was crushed to pass 40 mesh and after the fine fraction (−200) was screened off, the light minerals were removed by floation with methylene iodide (specific gravity 3.3). The heavy concentrate consisted of cerite and bastnaesite. The free grains of yellow bastnaesite were removed by hand-picking. The remaining grains that contained both cerite and bastnaesite were crushed and separated into two fractions, one −80+100 mesh, and another, −100+200 mesh. These fractions were separated by passing them through the Frantz isodynamic magnetic separator. The optimum tilt and pitch of the separator, which were slightly different for each of the two size fractions, were determined by trial. After the two fractions were passed through the separator nineteen times and recombined with the fine fraction, the remaining 4 grams of cerite were considered sufficiently pure for chemical analysis.

Table 5. Chemical Analysis of Cerite from Mountain Pass, San Bernardino County, California

Constituent	1	2	3	4
Ce_2O_3	35.73		37.3	.397
La_2O_3 etc.	31.53		32.9	.350
SiO_2	18.46	2.00	17.2	1.000
CaO	3.72		3.9	.24
MgO	1.58		1.6	.14
H_2O^-	0.14	0.14		
H_2O^+	2.26		2.4	.46
CO_2	3.56		3.7	.30
F	1.60		1.7	.31
Al_2O_3	0.95	0.95		
Fe_2O_3	0.76	0.76		
TiO_2	0.07	0.07		
Na_2O	0.20	0.20		
K_2O	0.13	0.13		
MnO	0.17	0.17		
BaO	0.37	0.37		
SO_3	0.12	0.12		
Total	101.35		100.7	
Less O=2F	−0.67		−0.7	
Corr. total	100.68		100.0	

1. Gross analysis on purified sample; M. K. Carron, analyst.
2. Subtractions for impurities: 1 per cent SiO_2 as chalcedony; 3.28 per cent SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Na_2O, K_2O and MnO as altered acmite and unidentifiable alteration products; 0.49 per cent BaO and SO_3 as barite; 0.14 per cent $H_2O(-)$ as moisture.
3. Corrected analysis with fluocarbonate included, recalculated to 100%.
4. Mol ratios calculated from column 3, with SiO_2 set equal to 1.000. Molecular weight of La_2O_3, etc. is taken as 328.5.

The complete chemical analysis of cerite from Mountain Pass prepared as described above is given in Table 5, column 1. The analysis corrected for about 5 per cent of impurities (Table 5, column 3), is compared with previously reported analyses in Table 6. A quantitative spectrographic analysis of the rare earths was made by H. J. Rose, Jr.; the results are shown in Table 7.

The problem of assigning a formula to cerite has always been complicated both by the great difficulty of purification and by the inherent variability of composition of the mineral itself. Most troublesome in this regard is the intimate admixture of bastnaesite with cerite which is almost universal. It has not been possible to obtain an *x*-ray powder diffraction pattern of cerite that is completely free of bastnaesite lines, although the material from Mountain Pass purified for analysis shows

TABLE 6. CHEMICAL ANALYSES OF CERITE

Constituent	1	2	3	4	5	6
Ce_2O_3	37.3	32.97	24.06	33.25	33.65	31.37
La_2O_3, etc.	32.9	35.72	35.37	34.60	37.49	38.64
SiO_2	17.2	18.10	22.79	18.18	15.60	21.24
CaO	3.9	5.80	4.35	1.69	1.27	2.97
MgO	1.6	0.21			0.07	1.88
H_2O	2.4(+)	1.26	3.44	5.18	1.48	2.10
CO_2	3.7				7.86	.30
F	1.7				0.94	1.47
Y_2O_3		3.86				
Al_2O_3		0.32	1.26		0.50	
Fe_2O_3					0.28	0.43
FeO		1.54	3.92	3.18		0.68
MnO		0.22			0.15	
$(Na, K)_2O$					0.15	
Gangue			4.33			
Total	100.7				99.44	101.08
Less O=2F	−0.7				−0.40	−0.62
Corr. total	100.0	100.0	99.52	96.08	99.04	100.46

1. Cerite from California, from column 3, Table 5 (M. K. Carron, analyst); 4.9% impurities subtracted and recalculated to 100%.
2. Cerite from Colorado, J. G. Fairchild, analyst (Goddard and Glass, 1940); 23.8% impurities subtracted and recalculated to 100%.
3. Cerite from Bastnäs, G. Nordström, analyst (Nordenskiöld, 1873).
4. Cerite from Bastnäs, L. Kettner, analyst (Stolba, 1879).
5. Cerite from Kychtym (Urals) (Silberminz, 1929).
6. Cerite from Bastnäs, J. H. Scoon, analyst (Gay, 1957*b*).

NOTE: An analysis of cerite from Jamestown, Colorado, has also been published by Hanson and Pearce (1941), but is not considered here because of the questionably high percentage of alumina (14.6%) reported.

bastnaesite lines in its powder pattern only in traces. We are faced with the question, therefore, of whether the fluocarbonate which usually appears in the analyses is to be wholly associated with bastnaesite, or partly with bastnaesite and partly with cerite. The presence of minor amounts of other impurities can also be seen optically in the Mountain Pass material as a finely disseminated phase, perhaps a fine-grained alteration product, penetrating the cracks and fissures in the cerite grains. The nature of these impurities is unknown, but their influence on the analytical data is probably minor.

Table 7. Spectrographic Analysis of the Total Rare Earths Extracted from Cerite of Mountain Pass, San Bernardino County, California
(H. J. Rose, Jr., Analyst)

	Wt. per cent of total rare earths
La_2O_3	22.40
CeO_2	54.30 (chemical)
Pr_6O_{11}	5.80
Nd_2O_3	17.30
Sm_2O_3	1.60
Y_2O_3	.69
Gd_2O_3	0*
	102.09

* Gd_2O_3 not detected; less than 1 per cent.

In attempting to interpret the chemical analysis of cerite in terms of the crystallography, it was assumed, first, that all of the fluocarbonate is included in the cerite formula; and, second, that none of it is included, but is to be subtracted from the analysis as bastnaesite. In the second case, no formula consistent with the crystallography and other evidence could be found, but, as will be shown, a satisfactory formula was evolved with the first assumption. For this reason, and also because, in the carefully prepared samples that were analyzed no significant amounts of bastnaesite could be detected by physical means, the following discussion is based on the assumption that fluocarbonate is an essential constituent of the cerite formula.

The crystallography places few restrictions on the composition of cerite because of the large size of the unit cell, but the following points must be considered. The molecular weight of the hexagonal cell contents as derived from the measured specific gravity is 11,000 ± 400. The rhombohedral symmetry demands that the largest formula weight be one-third of this, or 3780 ± 140. The only other restriction on the formula arises from the nature of the pseudo-cell, which is also rhombohedral but has a *c* axis one half of that of the true cell. We may conclude from the fact that the true cell is revealed by weak single crystal reflections which appear only above a moderately large Bragg angle, that the heavy atoms, at least, must occupy the pseudo-cell in multiples of 3. Therefore, we will expect the number of cations in the true cell to be present in multiples of 6.

TABLE 8. CHEMICAL COMPOSITION OF CERITE CALCULATED FROM UNIT CELL CONTENT

Component	Mountain Pass			Bastnäs		
	Formulas per cell	Wt. % calc.	Wt. % obs.[3]	Formulas per cell	Wt. % calc.	Wt. % obs.[4]
$(RE)_2O_3$[1]	24	70.3	70.1	24	69.7	70.0
CaO	7.5 } 12	3.7	3.9	6.4 } 12	3.2	3.2
MgO	4.5	1.6	1.6	5.6	2.0	2.0
SiO_2	32.5 } 42	17.6	17.2	42	22.3	22.6
CO_2	9.5	3.7	3.7			
F		1.6	1.7			
H_2O	13.2[2]	2.1	2.5	18	2.8	2.2
Mol. wt.	11,219			11,319		
Specific volume oxygen	19.9			19.9		
Specific gravity	4.78 (meas.) 4.86 (calc., *x*-ray) 4.87 (calc., optics)			4.89 (meas.) 4.92 (calc., *x*-ray) 4.91 (calc., optics)		
Formula:	$(Ca, Mg)_2(RE)_8(SiO_4, FCO_3)_7(OH, H_2O)_3$					

[1] RE represents Y, La, Ce, etc.

[2] 13.2 H_2O equivalent to 8.5 $H_2O+9.5\ (OH)^- = 18[(OH), H_2O]$

[3] From Table 6, column 1.

[4] From Table 6, column 6: 1.57 per cent bastnaesite and 4.70 per cent fluocerite subtracted and recalculated to 100 per cent.

In Table 8, the analysis of the Mountain Pass cerite and also the new analysis of the Bastnäs material reported by Gay (1957*b*) are interpreted in terms of the contents of the true hexagonal unit cell. It is found that the various conditions are met if Ca^{+2} and Mg^{+2} are in solid solution on the one hand, and $(FCO_3)^{-3}$ and $(SiO_4)^{-4}$ on the other, the latter with concomitant substitution of $(OH)^-$ for H_2O. In the Bastnäs analysis given in Table 6, column 6, 1.47 per cent F was reported with only 0.30

per cent CO_2, but because the silicate positions appear to be fully occupied by $(SiO_4)^{-4}$ groups, there is no way to fit this fluoride into the formula. Therefore, the excess F has been subtracted as fluocerite (somewhat arbitrarily) in Table 8. With these assumptions and adjustments it is found that a surprisingly good match is obtained in both cases for measured specific gravities, and those calculated both from unit cell contents and from refractive indices by the law of Gladstone and Dale (Jaffe, 1957). The formula proposed for cerite is:

$$(Ca, Mg)_2(RE)_8[(SiO_4)_{7-x}(FCO_3)_x][(OH)_x(H_2O)_{3-x}]$$

For the Mountain Pass sample, $x=1.6$ and for the Bastnäs material, $x=0$.

The substitutions postulated in the formula are uncommon, but not unprecedented. Because of the disparity in ionic radii, magnesium usually replaces calcium only in minor amounts, but in cerite the replacement apparently amounts to almost 50 mol per cent. Such replacement may be expected in structures where the calcium site involved is not a primary feature of the structure, and where adjustments are possible that will cause the coordination to become more nearly octahedral as the substitution of magnesium is increased. The best example of this type of substitution is garnet $(Ca,Mg_3Al_2(SiO_4)_3)$, in which extensive replacement is often evident. Gay (1957*b*) considers the calcium and magnesium to be in partial replacement of the rare-earth component, but the present indications of the analytical interpretation are that they play a separate role.

The hypothesis of the substitution of carbonate, or a fluocarbonate complex, for orthosilicate is more problematical, but not wholly unreasonable. A similar situation has been observed in apatite, which sometimes has been found to contain a considerable amount of carbonate. The role of carbonate in apatite (francolite) has been somewhat controversial (Palache, Berman, and Frondel, 1951, p. 882), but the only reasonable substitution mechanism would be the replacement of the tetrahedral PO_4^{-4} group by CO_3^{-2} or a tetrahedral combination such as $CO_3^{-2}+F^-$ or $CO_3^{-2}+OH^-$. The unusual apatites from Crestmore, California (wilkeite and ellestadite, Palache, Berman, and Frondel, 1951, pp. 905–6) indicate that PO_4^{-3}, SO_4^{-2}, SiO_4^{-4} and CO_3^{-2} may all replace each other extensively in the apatite structure. Although we accept the substitution of carbonate for silicate in cerite, the possibility that fluoride plays a role collateral with carbonate is less clear cut. In the Bastnäs analysis, where carbonate is insignificant, as stated earlier, there seems to be no way to fit the fluoride into the formula.

The formula proposed for cerite by Gay (1957*b*), $(Ca, Mg, RE)_3Si_2(O, OH, F)_9$, must be taken 20 or 21 times to fill the unit cell, and therefore must constitute only an approximation to the true formula. The formula presented by us, although satisfying all of the conditions imposed by the chemical, physical and crystallographic measurements, must also be regarded as tentative, in view of the assumptions and corrections made in interpreting the data. The true formula of cerite will probably be revealed only by a complete crystal-structure determination.

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HYDROTHERMAL SYNTHESIS OF WAIRAKITE AND CALCIUM-MORDENITE

L. L. Ames and L. B. Sand, *University of Utah, Salt Lake City, Utah.*

Abstract

The zeolites wairakite ($CaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$) and calcium-mordenite ($CaO \cdot Al_2O_3 \cdot 10SiO_2 \cdot 7H_2O$) were synthesized during the course of studies in the system lime-alumina-silica-water. The conditions for hydrothermal synthesis of these zeolites, their hydrothermal stabilities, and *x*-ray data are reported. The significance of these data is discussed, as it applies to the natural occurrence of wairakite and mordenite at Wairakei.

Introduction

During the course of studies in the system lime-alumina-silica-water, the zeolites wairakite (calcium-analcime) and calcium mordenite (ptilolite) were synthesized. The conditions necessary for syntheses approximate the natural environment found at the occurrence of these two zeolites at Wairakei, New Zealand.

Steiner (1953) has reported on the hydrothermal alteration at Wairakei. Types of rock being altered include tuffaceous sandstones, breccias, vitric tuffs and ignimbrite with the original composition of a plagioclase thyolite. Steiner divides the hydrothermal alteration at Wairakei into three zones characterized mineralogically by: 1) upper zone-clays of the montmorillonite group, 2) middle zone-zeolites, and 3) lower zone-adularia. Wairakite was reported by Steiner in cores from 600 to 2890 feet, constituting 2 to 15 per cent of the altered rock. The pH in the zeolite zone fluids was reported by him to be alkaline, with temperature and pressure ranges of 200 to 250° C. and 55 to 265 atmospheres.

Steiner (1955) also reported the physical and chemical properties of wairakite. Coombs (1955) has reported *x*-ray diffraction data on wairakite.

Previous Work on Calcium Zeolite Syntheses

Noll (1936*a*, *b*) first attempted to synthesize a calcium-analcime (wairakite). He used hydrated alumina, silica gel, and $Ca(OH)_2$ in solution in the ratio $CaO \cdot Al_2O_3 \cdot 4SiO_2$. This starting material was run at 300° C. and 87 atmospheres for between 15 and 24 hours. Noll stated that the phase formed could not yet be identified. These were the same P-T-time conditions which resulted in his successful synthesis of analcime.

Barrer (1950) attempted to synthesize wairakite by ion-exchange from analcime with limited success.

TABLE 1. CRITICAL HYDROTHERMAL RUNS ON THE CALCIUM COMPOSITIONS

Composition	T° C.	P (atm.)	Time	Phases
$CaO \cdot Al_2O_3 \cdot 10SiO_2$	330	1000	7	no crystallization
	350		5	mordenite
	380		5	mordenite
	395		5	wairakite+cash-I+cristobalite
	420		4	little crystallization
	435		3	little crystallization
	455		4	anorthite+cristobalite
$CaO \cdot Al_2O_3 \cdot 5SiO_2$	305	1000	3	little crystallization
	325		4	wairakite+cash-I+cristobalite
	360		4	wairakite+anorthite
	400		3	wairakite+anorthite
	420		4	anorthite
Ca-mordenite (Nova Scotia)	375	1000	5	mordenite
	385		5	mordenite+wairakite+cristobalite
	400		5	quartz+anorthite

METHODS OF INVESTIGATION

The pressure reactor vessels used were of the "test-tube" type described by Roy, Roy, and Osborn (1950). Runs were made under water pressures of 1000 atmospheres and temperatures from 200° C. to 560° C. The duration of these runs was from one day to one month.

Starting compositions were made by co-precipitating gels and using nitrates and silicic acid with calcination to 600° C. for 20 minutes. Equivalent results were obtained with both types of starting mixtures.

The phases were identified by *x*-ray diffraction analysis.

RESULTS

The critical hydrothermal runs are listed in Table 1.

For comparison, data on the sodium analogues are listed in Table 2. The results on the sodium compositions are in essential agreement with Barrer's work (1948).

TABLE 2. CRITICAL HYDROTHERMAL RUNS ON THE SODIUM MORDENITE COMPOSITION

Composition	T° C.	P	Time (days)	Phases
$Na_2O \cdot Al_2O_3 \cdot 10SiO_2$	180	saturated vapor	3	little crystallization
	200		2	mordenite
	300		1	mordenite
	330		1	albite+quartz

Table 3. Lattice Spacings and Visually-Estimated Relative Intensities on *X*-Ray Diffraction Powder Patterns

Hydrothermally-synthesized wairakite		Hydrothermally-synthesized calcium-mordenite	
d (Å)	I	*d* (Å)	I
6.81	4	13.4	3
5.57	9	10.47	1
4.83	4	9.10	8
3.64	3	6.61	8
3.41	10	5.79	1
3.21	2	4.95	1
3.05	1	4.54	5
2.90	8	4.00	6
2.784	1	3.82	6
2.675	4	3.48	10
2.488	5	3.39	4
2.414	3	3.22	9
2.275	1	2.89	2
2.214	3	2.71	1
2.115	1	2.56	3
2.000	1	2.44	1
1.987	3	2.370	1
1.856	2	2.268	1
1.822	1	2.124	1
1.732	4	2.043	1
1.706	1	1.955	1
1.680	1	1.885	2
1.653	1	1.804	1
1.613	1	1.547	1
1.586	2	1.530	1
1.489	1	1.480	1
1.473	1	1.445	1
1.438	1	1.380	1
1.409	3	1.300	1
1.352	3		
1.304	1		
1.279	1		
1.258	2		
1.239	1		
1,217	3		

X-ray diffraction data for the synthetic wairakite and calcium-mordenite are given in Table 3.

Discussion

Wairakite was not synthesized on composition $(CaO\cdot Al_2O_3\cdot 4SiO_2)$. The compositions $CaO\cdot Al_2O_3\cdot 5SiO_2$ and $CaO\cdot Al_2O_3\cdot 10SiO_2$ yielded wairakite, in the latter case as a decomposition product of calcium mordenite, while $CaO \cdot Al_2O_3 \cdot 4SiO_2$ and $CaO \cdot Al_2O_3 \cdot 6SiO_2$ compositions yielded a new transient phase CASH-I* through the temperature range of wairakite stability. $CaO \cdot Al_2O_3 \cdot 9SiO_2$ and $CaO \cdot Al_2O_3 \cdot 11SiO_2$ compositions did not crystallize through the wairakite stability range with runs up to 6 days in duration. Further, the composition $\frac{1}{2}Na_2O \cdot \frac{1}{2}CaO \cdot Al_2O_3 \cdot 5SiO_2$ yielded a cubic rather than a psuedo-cubic x-ray diffraction pattern, indicating that analcime is the stable phase on this composition. These results support the view of Steiner (1955) and Coombs (1955) who suggested very limited isomorphous substitution between analcime and wairakite due to the structural differences in these two supposed end members.

The presence of limited amounts of sodium would tend to lower the temperature of formation of wairakite, but whether limited isomorphous substitution of Na for Ca would lower the temperature of formation of wairakite a significant amount is hypothetical. The lower limit of formation of wairakite of 315° C. is suspect in any case, although the upper stability limit of about 400° C. probably is accurate to within ±10° C.

The synthesis of mordenite (ptilolite), on the other hand, furnishes a good example of a complete isomorphous series from a pure sodium to pure calcium mordenite. The stability range for the synthesis of sodium mordenite was found to be about 190° to 300° C., essentially the same range as reported by Barrer (2). The calcium mordenite was synthesized from about 340° to 380° C. Intermediate sodium-calcium mordenites were found to have intermediate upper stability limits.

An unusual aspect of this study was the failure to synthesize wairakite on composition ($CaO \cdot Al_2O_3 \cdot 4SiO_2$). Several unsuccessful attempts were made to synthesize wairakite from a $CaO \cdot Al_2O_3 \cdot 4SiO_2$ composition starting material. These included $CaO \cdot Al_2O_3 \cdot 4SiO_2$ plus various amounts of excess $Ca(OH)_2$, variation of the pH from 7 to 12 with the addition of NH_4OH, and the addition of varying amounts of sodium to the $CaO \cdot Al_2O_3 \cdot 4SiO_2$ starting material. The presence of excess silica in amounts greater than 0.5 mole and less than 1.5 moles is required for the synthesis of wairakite from the composition $CaO \cdot Al_2O_3 \cdot 4SiO_2$. Wairakite also was formed as a decomposition product of natural and synthetic mordenite ($CaO \cdot Al_2O_3 \cdot 10SiO_2 \cdot 7H_2O$). All of the natural zeolites studied (mordenite, heulandite and three clinoptilolites) initially decompose either to analcime or wairakite.

Steiner (1953) reports that ptilolite (mordenite) is the predominant mineral of the zeolite alteration zone at Wairakei, New Zealand, with some wairakite and heulandite.

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* Follows nomenclature of Rustum Roy (personal communication) who also has noted this phase.

These laboratory phase studies support the premise that excess silica is required for the formation of wairakite. Such an environment exists at Wairakei in the hydrothermally altered rhyolites. It is possible that wairakite is present at Wairakei as a decomposition product of mordenite, rather than as a primary phase.

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MINERAL HETEROGENEITY IN "GLAUCONITE" PELLETS*

J. F. Burst, *Shell Development Co., Houston, Texas.*

Abstract

The term "glauconite" is currently being used with a dual connotation. Originally coined (Gr. *glaukos* = bluish-green) as a description for a blue-green micaceous mineral, this word is now widely used as a rock term for small, spherical, sometimes green earthy pellets. By x-ray diffraction, those pellets can be grouped in four general mineralogical classes, only one of which has the diffraction properties of the mineral glauconite. These differences are not reflected in the size, shape, or color of the pellets.

In addition to unique x-ray properties, the mineral glauconite has been characterized by a lath-shaped micromorphology and by a restricted chemical formula which requires that at least two thirds of all possible potassium positions be occupied. A separate classification has been established for certain potassium-deficient structures on an order-disorder basis. In general, this division can be correlated with Yoder and Eugster's (1955) 1 M-1 Md division of low grade mica structures.

Introduction

The term "glauconite" has been used interchangeably for many years to describe a specific micaceous mineral as well as a particular morphological form. This dual usage results from the mineral species being found frequently in the form of small rounded greenish pellets. Careful mineralogical investigation of the pellets by petrographic and x-ray methods can readily distinguish the mineral glauconite from other similarly appearing materials (i.e. clay minerals). Geologists, however, who work in the field and whose studies of outcropping rocks and well samples are usually confined to binocular microscope investigation, rely essentially upon outward appearance for identification. This tends to pre-empt the morphological interpretation of the term glauconite.

In this manner, the designation "glauconite," originally defined as a mineral name, has become a "wastebasket" into which is placed almost any pellet that cannot be identified as a distinct mineral species of another kind, for instance, siderite or fluorapatite. *X*-ray work has shown rather conclusively that the term "glauconite" as it is commonly used is more often a generalization or, at best, a rock term rather than a precise mineral designation. It has been found that many materials termed "glauconite" in conversation and in the literature are actually composed of micaceous, chloritic, or montmorillonitic clay minerals.

One of the first descriptions of this material was by Alexander von Humboldt in 1823 [Schneider, Hyrum (1927)] who used the term *grün erde* to denote the occurrence of the green earthy material in sandstones and limestones throughout Europe. Equivalent designations of *terre*

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verte and *green sand* were made in other countries. Keferstein adopted the term "glauconit" (subsequently glauconite) in 1828 from the Greek *glaucos* = bluish-green and *ite* = resembling [Brown, R. W. (1954)]. It is not clear if the term at that time was a mineralogic or morphologic description, but the "ite" suffix by subsequent convention pressured for mineral interpretation. No attempt will be made to trace the history of glauconite literature in this report as this has been done on several previous occasions. For extensive bibliographies, references should be made to Schneider (1927), Hadding (1932), Gruner (1935), Steenhuis (1937–39), Hendricks and Ross (1941), Sabatier (1949), Smulikowski (1954), and Cloud (1955). Except where otherwise noted, the author of this report considers the term "glauconite" a morphological description because of the obvious inconsistency of defining the mineral glauconite as mineralogically heterogeneous.

ORGIN AND COMPOSITION

Classically, the mineral glauconite is a hydrous, iron-alumino silicate quite similar to members of the illite clay group. Actually it may be a highly ferriferous end-member composition within that group. Distinguishing chemical features include a K_2O content of 7–8 per cent and total iron of 20–25 per cent in which the ferric iron has been reported to exceed the ferrous by a multiple of 3 to 9. The average ferric-ferrous ratio in 34 sample analyses recorded in the literature was found to be 7.2 [Hendricks and Ross (1941); Hadding (1932)].

Important environmental interpretations have been drawn from this rather restricted range of ferric-ferrous ratios under the assumption that they reflect the redox potential (capacity to reduce or oxidize a system) in the environment where the glauconite formed. The particular range of values usually displayed by glauconite suggests a semioxidizing to semireducing environment. Several theories of origin –(1) fecal pellet conversion, (2) foraminiferal cavity-filling, (3) alteration of biotites, and (4) clay pellet agglomeration on the sea floor in response to undulating currents—can all be resolved by establishing the conditions of origin as requiring, simply, the silicate lattice, supplies of both potassium and iron, and a favorable oxidation potential.

An explanation for the association of glauconite with marine bioforms becomes apparent under these conditions. Decaying organic material (from dead animals or fecal mucous) creates a local reducing environment which sufficiently counteracts the over-all oxidizing marine environment to produce the semioxidizing conditions necessary to glauconite formation.

Alteration to glauconite of various silicates not in close association with decaying animal matter would be accomplished in a depositional area of natural semioxidizing conditions such as restricted basins or lagoons. Keller (1956) has recently described a green pelletal material from the Morrison Fm., Wyoming, which appears to be of lacustrine origin. Compared to most marine glauconites this material is highly aluminous, resembling the illites.

Theoretically, if there were only one set of environmental conditions pertinent to glauconite formation, its chemical and physical characteristics would be expected to be consistent. Variations in chemical analysis, and heterogeneity in mineralogical nature which has been recently noted [Burst (1952, 1953, 1954); Ehlmann (1954)] are probably due to different chemical environments. The most difficult contribution to evaluate is the iron ion. Most of the ancient glauconites which can be reliably designated as marine are highly ferriferous, suggesting that certain bottom dwelling organisms concentrate iron through digestive processes and deposit it with their fecal pellets.

Tarr (1920) suggested that the iron in glauconites is thrown down by oxidation. Still another suggestion maintains that glauconite is secondary after the high iron biotite lattice and does not require ferriferous contributions from the ocean waters. Although Galliher (1939) has found evidence of this with respect to the weathering of large biotite grains, the formation of glauconite by this method from heterogeneous marine sediments does not seem feasible. As most of these deep marine pellets appear to be converted fecal material, the suggestion is based on a selection process entailing an organism whose dietary habits enable the unerring segregation of biotitic and muscovitic lattices. Greenish colored fecal pellets found in the white sand beach at Gulf Beach, Florida showed little relation to either biotite or muscovite. Other fecal materials and Recent glauconites have been noted deficient in both iron and potassium.

Smulikowski (1954) agrees with a potassium deficiency in Recent and Tertiary glauconites; however, he often notes an excess of ferric iron. According to him, the formation of glauconite in Recent seas probably occurs at a stronger, on the average, concentration of ferric iron, than in seas of previous geological epochs. At the same time less interlayer cations (chiefly potassium) are now adsorbed by glauconite in the course of formation, than was generally possible in older geological epochs, especially the Paleozoic epoch. This would mean that the geochemical conditions at the sea bottom, in places favorable for glauconite formation, have undergone during the whole geological history a continual evolution in the direction of a growing concentration of iron and decreasing concentration of potassium.

Conway (1942) also notes the deficiency of potassium in clays of Recent and Tertiary ages, as well as in the sea water of these epochs. Actually, he plots a potassium content versus geologic time graph showing this effect.

The present author suggests that both iron and potassium experience oriented migration to favorable concentration centers within defective three-layer clay lattices. The mobility of the iron atom is well recognized through its occurrence in sedimentary deposits as siderite, pyrite, and marcasite concentrations. Its ability to segregate is demonstrated adequately by the ironstone concretion frequently found in essentially iron-free fire clays.

PREPARATION OF ORIENTED DIFFRACTION SLIDES

Pelletal purity is essential to glauconite classification on a mineral basis. The extreme difficulty involved in extracting pure glauconite pellets from sediments often results in imperfect separation which, in turn, leads to x-ray and chemical analyses of materials which are essentially glauconite pellets, but which have significant, although minor matrix impurities. It has been found absolutely necessary to hand-pick every pellet used for analysis. Particle weights listed in Table 1 are indicative of the difficulty involved.

TABLE 1. "GLAUCONITE" PELLET SIZES

Average of 10 pellets in milligrams

Celadonite (Italy)	1.677	Carrizo Fm. (Texas)	0.056
Navesink Fm. (N.J.)	0.477	Wilcox Fm. (La.)	0.044
Franconia Fm. (Wis.)	0.273	Wilcox Fm. (Texas)	0.037
Winona Fm. (Ala.)	0.211	Gatchell S.S. (Calif.)	0.031
Weches Fm. (Texas)	0.085	Rio Negro Fm. (Ven.)	0.009
Bashi Fm. (Ala.)	0.072	Tibu Fm. (Ven.)	0.009
Reklaw Fm. (Texas)	0.056	Pierson Glauc. (Texas)	0.008

To cope with this time-consuming task, micromethods for both chemical and x-ray oriented slide techniques were used. Both analyses can be accomplished with approximately 50 milligrams of material. SiO_2, R_2O_3, and water loss are measured gravimetrically, MgO and CaO titrametrically, K_2O and Na_2O spectrochemically, and ferrous and ferric iron colorimetrically.

An oriented clay slide is made with about five milligrams of material by introducing it into a miniature sedimentation column mounted directly on a microscope slide. After settling, excess liquid is decanted and the column removed from the slide leaving the one-dimensional "crystal" for irradiation.

X-RAY CLASSIFICATION

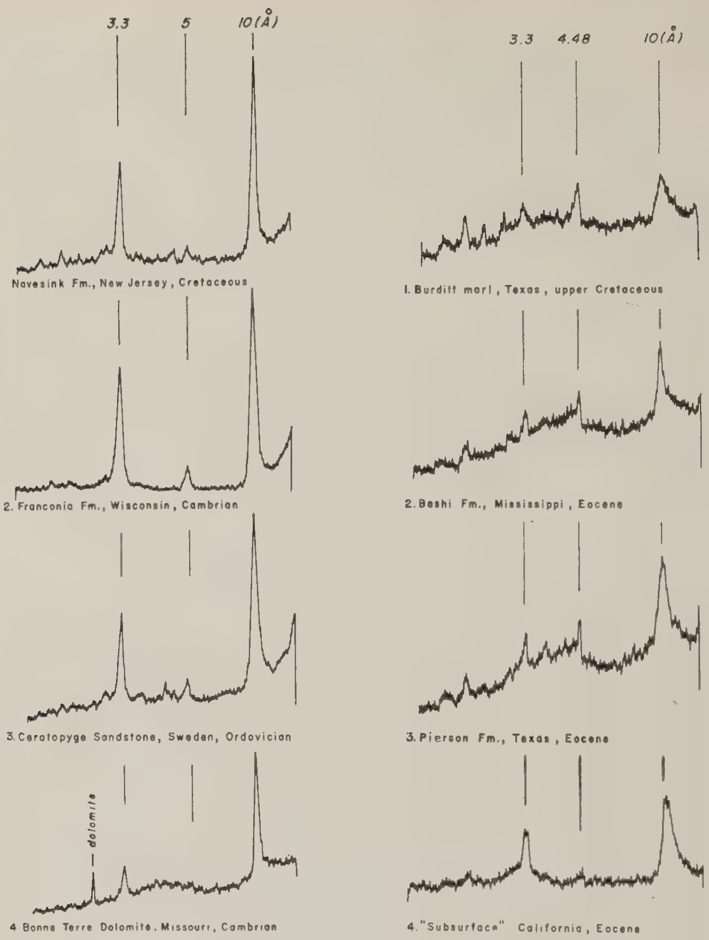
Neither size, nor shape, nor color can be used to distinguish pellets of the mineral glauconite from the many pellets which qualify as glauconite on a morphological basis. Materials of different sizes, shapes, and colors can have the same mineralogy, whereas other materials which are apparently similar morphologically have been found dissimilar mineralogically.

In this report, therefore, the small, rounded, green pellets, defined from a morphological point of view as glauconites are being reclassified into four major groups on the basis of *x*-ray analysis. The first group contains those materials which possess the structural properties generally attributed to the mineral glauconite. These properties are represented in Fig. 1a as three basal diffraction peaks of the micaceous 10-angstrom lattice. The relative intensities of the 10-, 5-, and 3.3-angstrom lines as well as their sharp symmetrical appearances are the most obvious diagnostic criteria in this type of analysis. The second group is also micaceous and monomineralic. The peaks, however (Fig 1b), are subdued, displaying broad bases and asymmetric sides. This suggests a less rigorous structural scheme and possibly a more moderate impress of formational environment.

Interlayered clay-mineral pellets are accommodated in a third group (Fig. 2) without differentiation as to the nature of the layer intercalation. It was found that most glauconite pellet forms contain interlayered material to some degree. A fourth group (Fig. 3) has been established for the many instances of mineral mixture found in pellet form. Most frequent combinations are illite with montmorillonite and illite with chlorite. No separate classification has been established for pellets containing minerals which could be classified as impurities (i.e., quartz, calcite).

Recently Levinson (1955) and Yoder and Eugster (1955) have shown that mica polymorphic classifications can be extended to relatively disorganized structures strikingly similar to glauconite lattices. These are the 1 M and 1 Md polymorphs obtained experimentally at low temperatures and generally accepted as being the most likely stability fields for sedimentary micas.

A survey of the glauconites in random powder mounts proved that the so-called ordered and disordered groupings can be similarly made on the basis of 1 M and 1 Md classification. Each of the glauconitic materials can be classified as single-layer monoclinic mica with the degree of single-layer crystallinity varying between 1 Md and 1 M. Franconia glauconite and Navesink glauconite (New Jersey greensand) appear to have 1 M structures (Fig. 4). There are insufficient reflections to entirely satisfy



Navesink Fm., New Jersey, Cretaceous

2. Franconia Fm., Wisconsin, Cambrian

3. Ceratopyge Sandstone, Sweden, Ordovician

4 Bonne Terre Dolomite. Missouri, Cambrian

1. Burditt marl, Texas, upper Cretaceous

2. Bashi Fm., Mississippi, Eocene

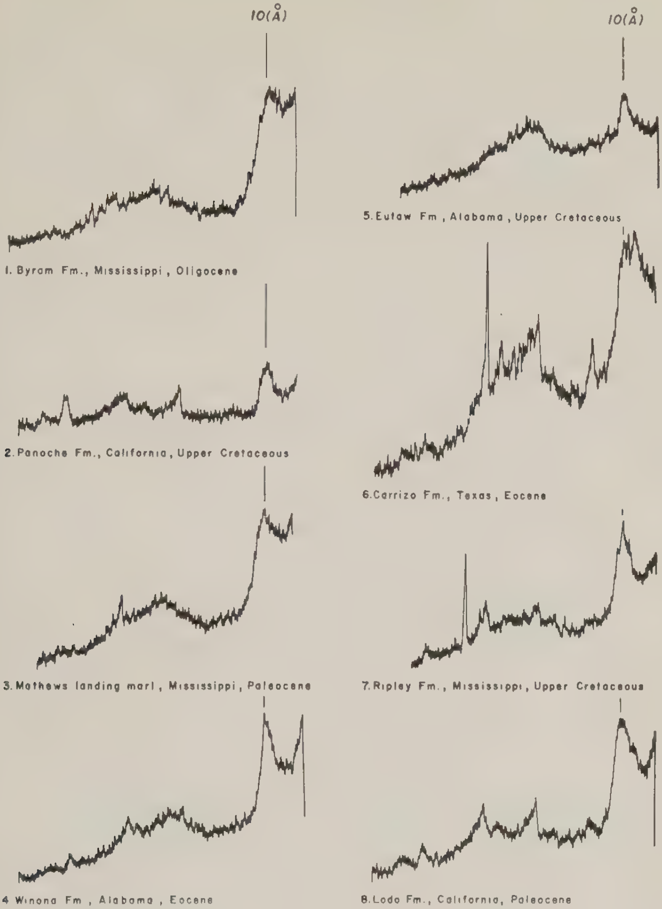
3. Pierson Fm., Texas, Eocene

4. "Subsurface" California, Eocene

FIG. 1. *X*-ray diffractograms of glauconites. (a) Left: well-ordered; (b) right: disordered.

the 1 M data such as listed by Yoder and Eugster (1955); however, more lines are present than the 1 Md classification would permit. Conversely, Pierson glauconite seems to be fairly representative of the 1 Md type mica structure. Basal reflections are extremely low. The 4.48-Å region is smeared out in the asymmetry typically indicative of disorder and the 2.55- to 2.58-Å reflections appear more or less broad and diffuse.

The 1 Md or disordered lattice is not readily apparent in the Bashi glauconite which had been classified as disordered by virtue of the diffraction relationships observed on patterns resulting from oriented flake-type sample mounts. The Bashi, however, is noted as the least



1. Byram Fm., Mississippi, Oligocene

2. Panoche Fm., California, Upper Cretaceous

3. Mathews landing marl, Mississippi, Paleocene

4 Winona Fm, Alabama, Eocene

5. Eutaw Fm, Alabama, Upper Cretaceous

6. Carrizo Fm., Texas, Eocene

7. Ripley Fm., Mississippi, Upper Cretaceous

8. Lodo Fm., California, Paleocene

FIG. 2. *X*-ray diffractograms of interlayered glauconites.

disordered of the disorder type glauconites; therefore, it is quite possible that its pattern would more resemble the ordered lattice type than other materials farther down on the disorder scale.

Estimates of order-disorder relationships are not significantly different, regardless of which type of sample mount is used—oriented aggregate or random powder. The dividing line between the ordered and disordered structures was however, more difficult to approximate if only the random powder patterns were taken into consideration and may be more or less obscured by impurities such as the small calcite accessory in the Burditt specimen.

General correlation between the two types of sample mounts was

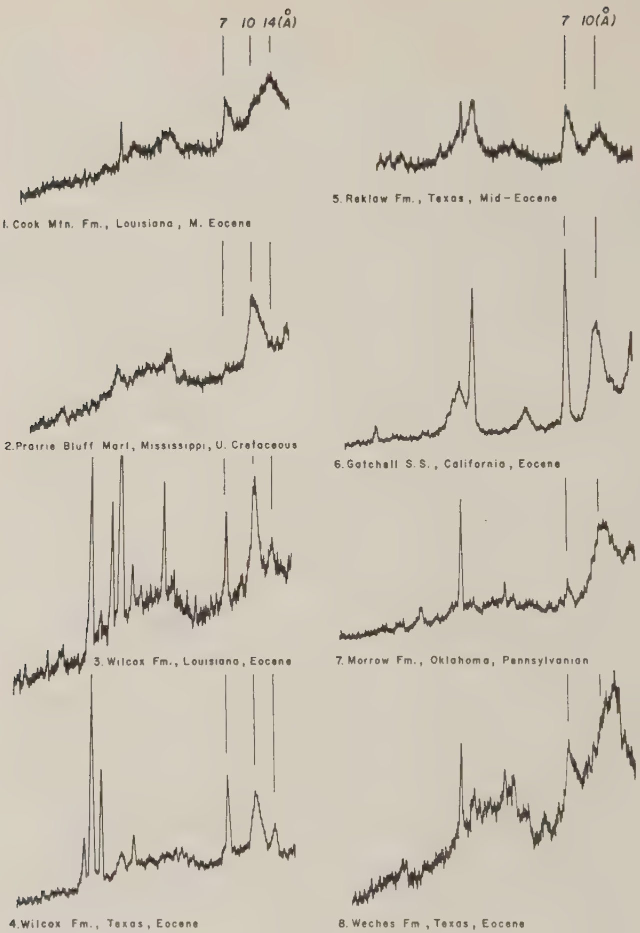


FIG. 3. *X*-ray diffractograms of mixed-mineral glauconites.

made possible due to imperfect orientation of clay platelets. The oriented flake sample is designed to eliminate (*hkl*)'s and consequently, to eliminate the characteristics of randomness on *x*-ray diffraction patterns. Perfect orientation of the flakes, however, is not realized, and a few of the disoriented layers are in a position to reflect (*hkl*)'s even though the sample has been oriented for reflections of basal spacings only.

The fact that the 4.48-Å reflection can be eliminated in the so-called ordered glauconites by orientation and, seemingly, cannot be eliminated from the patterns in the disordered glauconites suggests that, although the orientation in each of the sample types is comparable, disorder may provoke some departure from planarity in the grossly oriented structures.

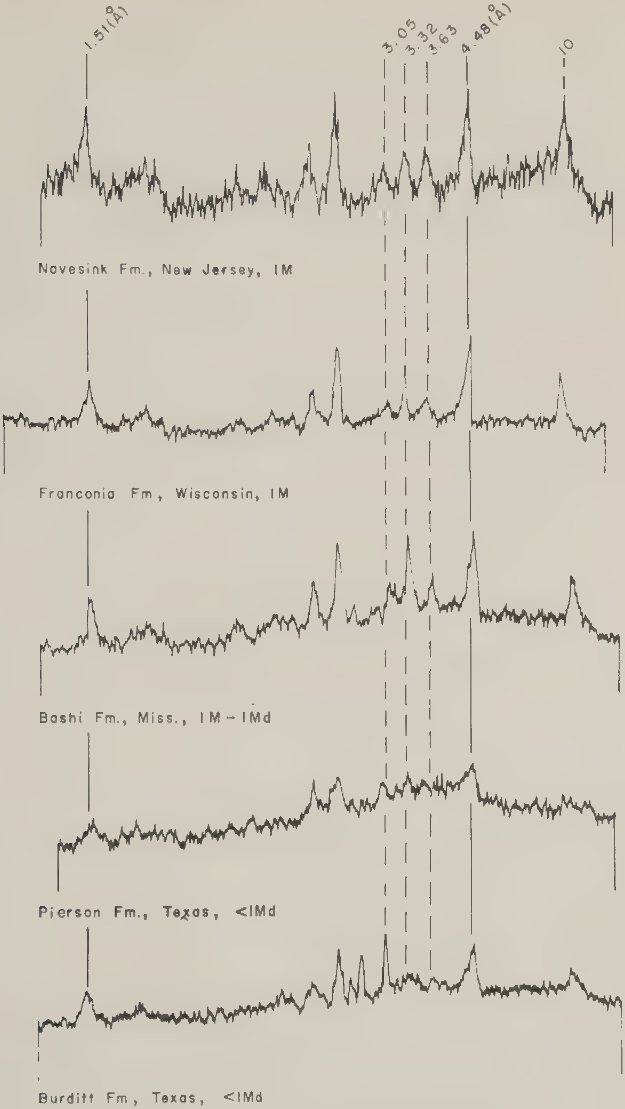


FIG. 4. Mica polymorphs in glauconite.

Chemical Classification

Obtaining chemical analyses of glauconitic materials can become a very difficult task owing to problems of availability, concentration, and purity. Except for those well-documented and classical glauconite exposures which yield the materials frequently described and redescribed in the literature, few glauconitic beds contain pellets in sufficient proportion to allow the accumulation of the quantities necessary for analytical study by any easy method. Large quantities of sample material are usually required to produce a small quantity of glauconite pellets. In the petroleum industry, however, glauconitic material about which mineralogic information is desired must be extracted from the usually small downhole sample recoveries. This necessitates the adaptation of microanalyses, both *x*-ray and chemical, to the glauconite work.

Table 2. Glauconite Chemical Analyses in Weight Per Cent

	1	2	3	4	5	6	7	8	9	10
SiO_2	53.22	35.67	48.0	52.7	48.66	47.1	49.0	51.7	51.5	47.5
Al_2O_3	21.19	14.56	10.7	13.7	8.46	11.5	8.4	10.9	23.6	15.45
Fe_2O_3	1.22	3.03	18.0	9.5	18.80	16.00	20.0	14.5	10.0	13.4
FeO		23.23	3.9	5.0	3.98	8.00	2.4	4.3	3.7	3.15
MgO	6.02	9.24	3.0	3.5	3.56	3.6	4.0	4.5	2.00	2.9
CaO		1.13	3.0	.3	.62	1.3	.3	.000	.06	1.2
K_2O	11.20	8.06	7.8	8.2	8.31	8.2	7.0	6.15 avg.	4.8	6.4
Na_2O	.34	.49	.18	.1	0.00	.2	.18	.23	.62	.16
$H_2O^{1000-100°C}$			7.4	6.8	6.56	6.44	7.5	6.9	4.7	11.1
Total			101.98	99.80	99.80	102.34	98.78	99.18	100.98	101.26

1. Alurgite [Grim *et al.* (1937)].
2. Biotite [Gruner (1935)].
3. Navesink Fm., N. J. Greensand, Cretaceous.
4. Ceratopyge Sandstone, Sweden, Ordovician.
5. Bonne Terre Fm., Missouri, Cambrian [Hendricks and Ross (1941)].
6. Franconia Fm., Wisconsin, Cambrian.
7. Bashi Fm., Alabama, Eocene.
8. Pierson Fm., Texas, Eocene.
9. "Subsurface," California, Eocene.
10. Burditt Marl, Texas, Upper Cretaceous.

A combination of general microchemical techniques for the components (Table 2) silicon, R_2O_3, magnesium, and calcium, spectrochemical techniques for sodium and potassium, and colorimetric techniques for ferrous and ferric iron has been developed for use on samples of less than 50 mg. and has been used to construct the chemical formulas shown in Table 3 for various of the glauconites studied. The formulas are based on an idealized unit cell of 24 oxygen atoms which can accommodate, after allowances for hydrogen, 44 cationic valences. These must be distributed among the materials contained in the elemental analysis to effect neutrality [Kelley (1945)]. It has been found that separating the potassium atomic equivalence from the so-called exchange ions (sodium and calcium) when writing the formulas provides a convenient method for the comparison of *x*-ray and chemical data.

It is interesting to note in comparing Table 3 with Fig. 1 that those materials which display the *x*-ray diffraction patterns of well-ordered single-layer micaceous materials consistently contain more potassium than do those materials which possess disordered mica structures. When the potassium atom equivalent falls below approximately 1.4 per unit cell, ordered stacking becomes less apparent owing to the decreased binding power normally supplied to the lattice by potassium. True randomness of the montmorillonite stacking type becomes evident in the low potash glauconites with the appearance of the aforementioned 4.48-Å reflection signifying a two-dimensional diffractor. Apparently, disordering begins when fewer than two out of every three possible potassium positions are filled. Peak broadening and asymmetry result.

TABLE 3. CALCULATED FORMULAS FOR ORDERED AND DISORDERED GLAUCONITES

Ordered Glauconites	Bonne Terre Fm., Missouri, Cambrian $\mathrm{K_{1.58}(Ca)_{0.10}(Al_{0.70}Fe'''_{2.11}Fe''_{0.49}Mg_{0.82})(Si_{7.22}Al_{0.78})O_{20}(OH)_4}$
	Franconia Fm., Wisconsin, Cambrian $\mathrm{K_{1.52}(Na,\ Ca)_{0.27}(Al_{0.81}Fe'''_{1.74}Fe''_{0.97}Mg_{0.79})(Si_{6.85}Al_{1.15})O_{20}(OH)_4}$
	Ceratopyge Fm., Sweden, Ordovician $\mathrm{K_{1.48}(Na,\ Ca)_{0.06}(Al_{1.74}Fe'''_{1.02}Fe''_{0.59}Mg_{0.77})(Si_{7.47}Al_{0.53})O_{20}(OH)_4}$
	Navesink Fm., New Jersey, Cretaceous $\mathrm{K_{1.43}(Na,\ Ca)_{0.51}(Al_{0.81}Fe'''_{1.97}Fe''_{0.47}Mg_{0.66})(Si_{6.99}Al_{1.01})O_{20}(OH)_4}$
Disordered Glauconites	Bashi Fm., Mississippi, Eocene $\mathrm{K_{1.32}(Na,\ Ca)_{0.10}(Al_{0.74}Fe'''_{2.23}Fe''_{0.30}Mg_{0.89})(Si_{7.28}Al_{0.72})O_{20}(OH_4)}$
	Burditt Fm., Texas, Upper Cretaceous $\mathrm{K_{1.20}(Na)_{0.09}(Al_{1.66}Fe'''_{1.47}Fe''_{0.40}Mg_{0.62})(Si_{6.98}Al_{1.02})O_{20}(OH)_4}$
	Pierson Fm., Texas, Eocene $\mathrm{K_{1.12}(Na)_{0.05}(Al_{1.25}Fe'''_{1.58}Fe''_{0.52}Mg_{0.95})(Si_{7.41}Al_{0.59})O_{20}(OH)_4}$
	"Subsurface," California, Eocene $\mathrm{K_{0.81}(Na,\ Ca)_{0.17}(Al_{2.53}Fe'''_{1.05}Fe''_{0.46}Mg_{0.41})(Si_{6.84}Al_{1.16})O_{20}(OH)_4}$

From these analyses, it would seem that Bonne Terre glauconite and Franconia glauconite represent an end-point mineral composition within the mica group to which the mineral name glauconite should be applied. Retreating from this end-point in gradual steps of diminishing potassium content are materials which less and less resemble glauconites and more and more resemble montmorillonites. That this change is transitional over a broad range of potassium values suggests that the potassium fixation is limited not by the capacity of the structure for such a phenomenon, but by the capacity of the depositional medium to supply potassium to the structure.

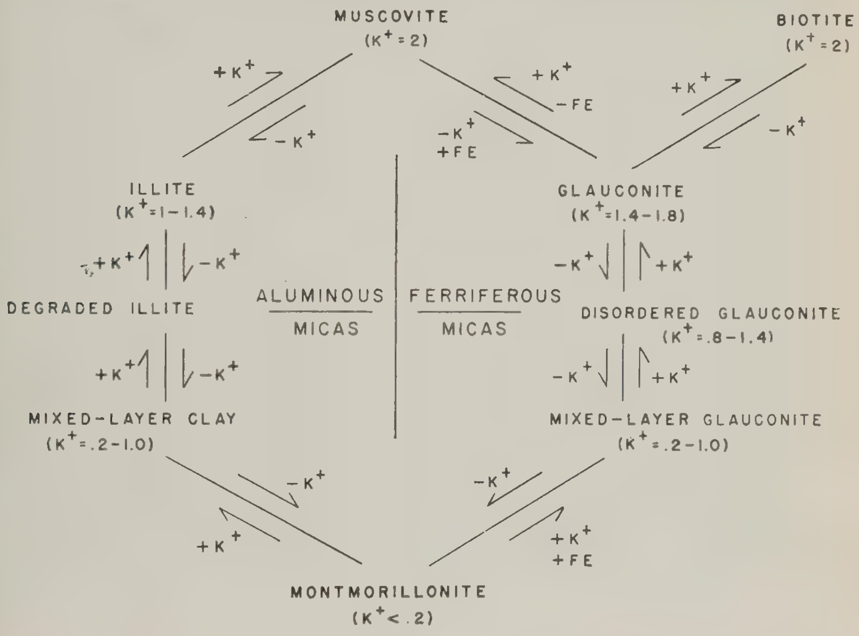
All of the materials are clearly dioctahedral. The value of cationic equivalence in the octahedral layer is surprisingly similar in the Franconia, Ceratopyge, and Bonne Terre. An excess of octahedral aluminum and a smaller ferric-to-ferrous iron ratio in the Ceratopyge differentiates it from the other three mineral representatives.

It appears that the potassium deficiencies of the clay minerals (mica-type) may be direct measures of impurity, assuming that mineral interlayering is considered an impurity. Other impurities, such as quartz or calcite, must be assessed by the observation of abnormal SiO_2 and CaO values. Kelley (1945), clearly established the conditions necessary to correct formula calculation: (1) It must be known that the sample is composed of material of a given lattice type; (2) the purity of the sample must be assured; (3) the chemical analysis must be reasonably accurate.

The designation of a certain degree of lattice randomness evidenced by its *x*-ray diffraction properties, as a particular glauconite type (i.e. disordered) may, of course, be questioned. The designation of end-members in isomorphous series is often difficult, and this particular composition may not be a true end-member. However, its frequent repetition among the many glauconites examined seems significant. It may quite possibly be a reflection of a particular chemical environment or set of chemical processes that frequently lead to the formation of a particular glauconite type.

The classification (see Fig. 5) of green micaceous pellets on the basis of potassium content has been used in an attempt to construct a parallelism between the poorly ordered high aluminum micas (illites) and the poorly ordered high iron micas (glauconites). Equivalent genetic stages have been designated for illite and glauconite; degraded illite and disordered glauconite; and mixed-layer clays and mixed-layer glauconites. All six stages are suggested as intermediate between true micas and true swelling clays. Biotite is included because of its high iron content and because direct observation of its conversion to glauconite has been reported [Galliher (1938)]. This change, however, requires the transformation of a trioctahedral lattice to low order dioctahedral.

Smulikowski (1954) divided glauconites in a somewhat similar manner, but reserved two names; illites and pholidoides for the highly aluminous materials. For instance, the Ceratopyge material described herein, displaying an excess of aluminum over ferric iron in octahedral coordination, a loss of potassium, and a total octahedral cationic equivalence just slightly above four would, under Smulikowski's system, be classified as illite. To him, pholidoides are similar to illites in having excess aluminum over magnesium in octahedral coordination, but differ in that the total octahedral cationic equivalence is considerable above 4 (by as much as 20 per cent). The differentiation, therefore, is made on a "seat of fixation charge" basis.



K^+ NUMBERS = ATOM EQUIVALENTS OF POTASSIUM PER LATTICE UNIT

FIG. 5. Suggested diagenetic relationships in micas.

MICROMORPHOLOGY

Electron micrograph monitoring of glauconite specimens provided an interesting parameter of glauconite mineralogy (Fig. 6). The well-ordered, high-potassium materials appeared as lath-shaped booklets. It further appeared that the best-developed laths occurred in Franconia and Bonne Terre materials where the individual rectangular plates displayed length-to-width ratios of about 5 to 1. This unique morphology

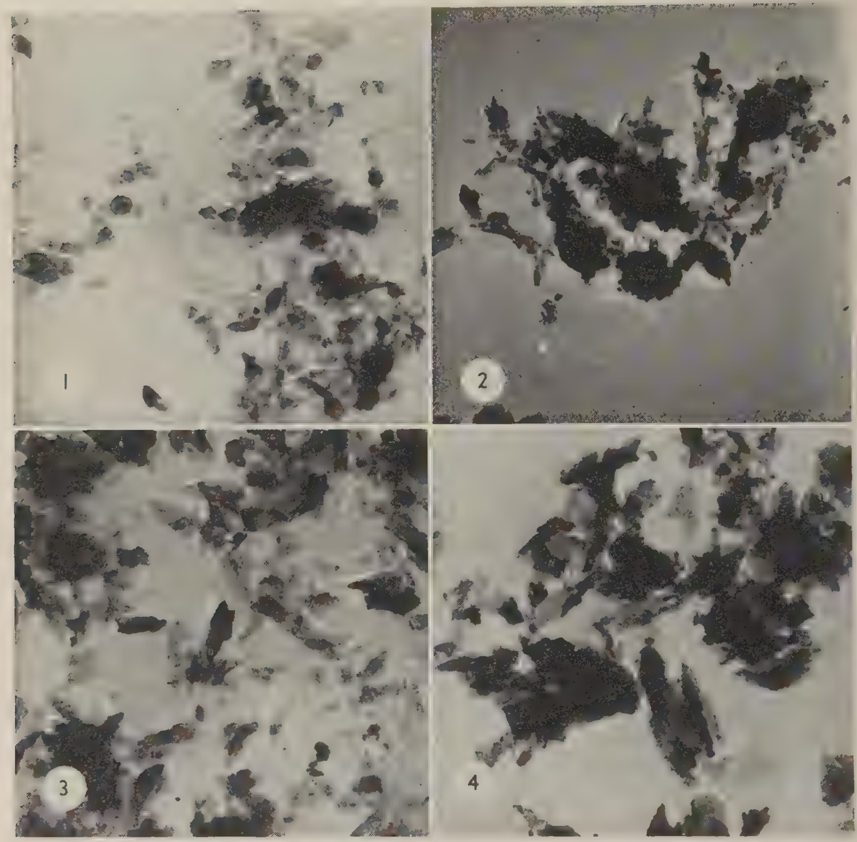


Fig. 6. Electron photomicrographs of well-ordered glauconites.
1. Navesink Fm., New Jersey, Cretaceous (×13,000).
2. Franconia Fm., Wisconsin, Cambrian (×11,000).
3. Ceratopyge sandstone, Sweden, Ordivician (×13,000).
4. Bonne Terre dolomite, Missouri, Cambrian (×10,000).

is another useful argument for the establishment of Bonne Terre and Franconia glauconites as type minerals.

Disordered glauconites and mixed-mineral pellets such as shown in Fig. 7 tend toward equilateral plates. Bashi glauconite, which has already been cited as resembling the ordered glauconites, shows a few elongated plates.

Conclusions

Students of glauconite have usually approached the problem with one of two different viewpoints. One group, usually field geologists or others making macroscopic or binocular microscopic examinations, describe

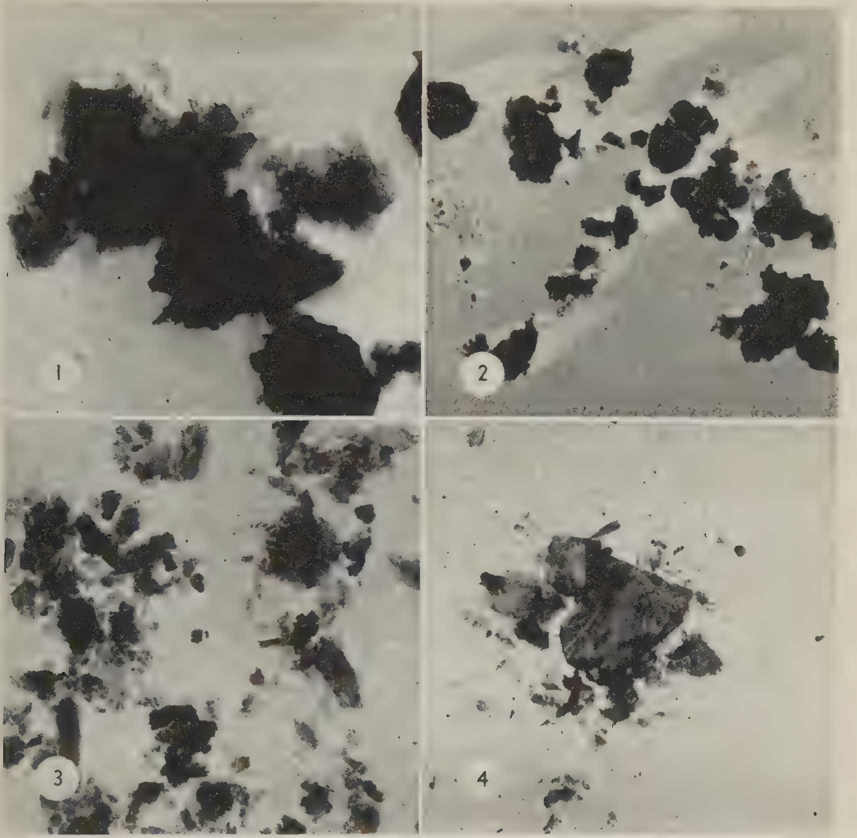


FIG. 7. Electron photomicrographs of disordered glauconites.
1. Gatchell sandstone, California, Eocene (×20,000).
2. Weches Fm., Texas, Eocene (×11,000).
3. Bashi Fm., Mississippi, Eocene (×13,000).
4. Pierson Fm., Texas, Eocene (×11,000).

all green, earthy pellet materials as glauconite, obviously a gross classification based on external appearance. The other, usually composed of laboratory analysts, confine the designation to monomineralic micaceous materials of slightly varying chemical composition and prescribe an average formula for the ideal mineral material. In this case, the description is a mineral term.

In this report, the earthy green pellets are divided into four groups by x-ray diffraction; one is a mineral genus and three are rock categories. The highest rank is restricted to materials which apparently approach the rigorous qualifications of specific mineral classification. Within this group, two materials, Franconia glauconite and Bonne Terre glauconite, are proposed as representative mineral types. These two materials may therefore be termed neotypes for glauconite. This group possesses unique chemical properties and unique disaggregate morphologies in addition to selective diffraction properties.

Two of the three remaining groups were established for glauconitic materials which apparently bear genetic relationships to the mineral type group, but differ somewhat in potassium content. The highest order of these two groups is considered submineralic because, although its slight potassium deficiency indicates interlayering, the repeated occurrence of this particular degree of interlayering suggests a classification higher than the randomness implied by a rock term. The other group of considerably potassium-deficient three-layer silicate lattices produces poor diffraction patterns and often displays swelling properties.

The fourth category is a designation for green colored clay pellets containing two or more argillaceous minerals.

The reclassification into four specific groups of heterogeneous materials previously described by a single name and often considered mineral equivalents can be used to advantage in stratigraphic and environmental interpretations. It is deemed necessary that "glauconite" designations and classifications be made with the assistance of x-ray diffraction just as is required by other clay-mineral identifications. Morphological descriptions which result from hand-specimen examinations often conceal significant mineral characteristics.

Acknowledgments

The author is greatly indebted to many geological and mineralogical workers both in the United States and abroad who very generously contributed specimens and personal observations on glauconite occurrence to this endeavor. Particular appreciation is due Mr. Drayton B. Speights, University of Houston; Dr. D. E. Feray, Dallas, Texas; Dr. E. D. Goldberg, Scripps Institution of Oceanography; and Mr. E. H. Rainwater, Mr. E. J. Theesen and Dr. H. B. Stenzel, Shell Oil Company, for their help.

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THE CRYSTAL CHEMISTRY OF SCAWTITE

DUNCAN MCCONNELL,* *Ohio State University, Columbus, Ohio*
AND
JOSEPH MURDOCH, *University of California at Los Angeles, California.*

ABSTRACT

The crystal chemistry of scawtite is interpreted on the basis of a new chemical analysis, together with crystallographic and physical measurements on material from Crestmore, California.

Although no clue to the probable structure is obtained, it is evident that the principal cation (calcium) is not stoichiometrically related to either anion (silicate or carbonate) but rather to their sum. Water (as hydroxyl ions) is an additional complication of minor significance.

It is deduced that the smallest symmetrical unit contains 48 oxygen atoms and that carbon displaces silicon in this structure in the same general manner as has been postulated for the displacement of phosphorus by carbon in carbonate apatites.

INTRODUCTION

Any attempt to resolve the question of the crystal chemistry of a mineral as complex as scawtite must judiciously employ the meager data available and simultaneously consider all reasonable theories that may be applicable. At the outset, the difficulties should not be minimized. Considering the grosser aspects of the chemical data, it becomes apparent that certain cations are essential to this structure: calcium, silicon, carbon, and possibly hydrogen. More careful scrutiny of the analyses leads to the conclusion that no reasonably close approximation to a constant ratio obtains for any two of these cations. Obviously a determination of the structural equivalence of certain cations might contribute significantly to an understanding of the crystal chemistry of this substance.

ANALYTICAL DATA

Two chemical analyses of scawtite have been recorded previously, one by Hey (Tilley, 1930) and another by Scoon (J. D. C. McConnell, 1955). A third analysis is reported here; it is by Goldich and Ingamells. The difficulties of isolating an adequate quantity of pure material have necessitated semimicro methods for certain constituents in several instances. Although it must be admitted that the precision of the analyses may be somewhat less than might be desired, nevertheless, the work has been diligently performed by persons of recognized ability. Therefore significant differences, such as the following, cannot be dismissed because of lack of mutual agreement. Particular attention is directed to the silica and carbon dioxide of Table 1. It is noticeable that there must exist some type of inverse relationship between the amounts of these constituents. (We cannot suppose that a result for silica would contain an error as great as 20 per cent of the amount present and simultaneously contain an error for volatile constituents as great as 200 per cent of the amount present.) It is essential, therefore, that the chemical data be accepted at face value. That is, any acceptable interpretation must be generally consistent with all of the chemical data.

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* Special Research Fellow, National Institute of Dental Research, U. S. Public Health Service.

Table 1. Analyses of Scawtite

	Scawt Hill (Hey)	Ballycraigy (Scoon)	Crestmore (Goldich-Ingamells)
CaO	46.4	46.1	46.93
SiO_2	34.2	43.5	41.95
CO_2	18.0	4.4	5.6
H_2O*	—	4.4	4.96
Others*	—	1.2	0.39
	98.6	99.6	99.83

* For Scoon's analysis: $R_2O_3=1.2$; of total water 0.1 was below 105° C. For the analysis by Goldich and Ingamells: $MgO=0.16$, $Al_2O_3=0.14$, total iron as $Fe_2O_3=0.07$, $MnO=0.01$, $TiO_2=0.01$, of total water 0.06 was below 105° C. Further tests indicated: P_2O_5 absent or small, Na_2O and K_2O each less than 0.1 per cent.

Interpretation of Analytical Data

As an initial premise, we are concerned with the question of the substitution of CO_3 groups for SiO_4 groups, as has already been postulated as the probable mechanism for the occurrence of carbon dioxide in carbonate apatites (McConnell, 1952). As previously supposed, the number of oxygen atoms of the entire structure remains fixed, and the symmetrical arrangment is essentially preserved despite very small displacements necessary to form 4 CO_3 groups from oxygens that would otherwise comprise 3 SiO_4 groups. In the case of apatite, the general structure of which is well known, it has been feasible to assume specific loci for the substitution of carbon that are consistent with these general symmetry requirements. In the case of scawtite this is impeded by a lack of knowledge of the structure.

Inasmuch as the crystalline symmetry of silicate structures is determined essentially by the arrangment (or packing) of the oxygen atoms, it is permissible to assume that the number and arrangment of oxygen atoms is the same for all three samples of scawtite that have been analyzed.

The number of oxygen atoms per structural unit can be resolved by a method previously indicated (McConnell, 1954a) provided accurate measurements of the lattice and the specific gravity are available in addition to the chemical data. Although these calculations cannot be accomplished, in the absence of *x*-ray diffraction data for the original material (Tilley, 1930), nevertheless, such calculations can now be made for the material from Crestmore (Murdoch, 1955) and, with slightly less certainty, for the material from Ballycraigy (J. D. C. McConnell, 1955). The uncertainty in the latter case depends upon whether the reported specific gravity is merely a quotation of the determination by Tilley (1930) or represents a new determination.

Calculation of the number of oxygen atoms gives the following results:

Crystallographic data by	*Sp. gr.*	*Oxygens*
J. D. C. McConnell	2.77	46.0
J. Murdoch	2.71	47.1

Specific gravity determinations by one of us (J.M.) gave 2.707 (with the Berman balance) and 2.714 (with a pycnometer) at room temperatures.

A prime number as large as 47 is highly improbable. We conclude that the scawtite structure contains 48 oxygens rather than 46, which contains merely a factor of two and another moderately large prime number. This number (48) is the total number of oxygens, including any that occur with hydrogen bonding. Furthermore, it is assumed, in view of energy considerations, that all spaces large enough to be occupied by oxygen atoms are filled; that is, there are no large "holes" in the structure.

Were it possible to discover an analogous structure having similar periodicities, optical properties, etc., a fairly straightforward approach to the crystal chemistry of scawtite would be possible. However, scawtite does not appear to resemble any known structure closely. It shows no resemblance to xonotlite, as suggested by J. D. C. McConnell (1955), for example, either in lattice dimensions or optical properties.

The refractive indices are similar to those of tremolite, and it is possible that the structure of scawtite is composed of double chains of silicate tetrahedra, but neither the orientation nor the periodicities of such chains are suggested by the lattice dimensions obtained by Murdoch (1955) or J. D. C. McConnell (1955)

Allocating the charges of the cations to the 48 oxygen atoms in the proportions indicated by the chemical analyses gives the following results

	Crestmore	*Ballycraigy*	*Scawt Hill*
Ca	14.58	14.54	14.26
Si	12.10	12.80	9.82
C	2.22	1.76	7.04
H	9.54	8.64	—

Except for the material from Scawt Hill, it is noticeable that the sums of the silicon and carbon atoms are approximately the same as the numbers of calcium atoms, but the number of hydrogen atoms is about 9.5 for the Crestmore sample, but merely 8.6 for that from Ballycraigy. Unfortunately very little can be concluded concerning the material from Scawt Hill except that it must be considerably lower in water. If then, the tremolite formula is taken as a guide and is written in its most general form $X_7(OH)_2Si_8O_{22}$, and the substitution of carbonate groups $3SiO_4 \rightarrow 4CO_3$ is considered, this formula can be rewritten in doubled form as $Ca_{14}(OH)_4(Si_{16-x}C_{4x/3})O_{44}$, in which case it has 48 oxygen atoms (the probable number in scawtite). In case hydrogens occur in excess of those necessary for the four hydroxyl groups, a concomitant diminution of silicon atoms is taken as evidence of the occurrence of tetrahedral hydroxyls (McConnell, 1954b and 1956) and requires further modification of the formula, thus $Ca_{14}(OH)_4(Si_{16-x-y}\ C_{4x/3}\ H_{4y})O_{44}$. The next question is how this general formula fits the chemical analyses of scawtite. In Table 2, then, the subscripts for the derived tremolite formula are given for the scawtite analyses.

TABLE 2. CATION CONTENTS CALCULATED FOR 48 OXYGEN ATOMS

	Crestmore	Ballycraigy	Scawt Hill
Ca	14.58	14.54	14.26
H_4 (of $(OH)_4$)	1.00	1.00	—
Si	12.10	12.80	9.82
$C_{4/3}$	1.66	1.32	5.28
H_4 (tetrahedral)	1.38	1.16	—
Σ (tetrahedra)	15.14	15.28	15.10

Although it cannot be asserted that the Ca to Si ratio is 7:8 (as in tremolite), fairly good results are obtained if the carbonate, silicate and excess hydroxyl hydrogens are summed according to the methods outlined. Particularly, this is true for three samples that gave 18 and 4.4 per cent as their maximum and minimum carbon dioxide contents. This can hardly be a fortuitous relationship despite the fact that it was obtained by indirect methods.

CONCLUSIONS

Thus, although the ratio of Ca to anionic groups in scawtite cannot be decided—there being two possible choices, 7:8 or 1:1—there can be little doubt that the carbon dioxide enters the structure as triangular groups in such a manner that the amount is variable and that silicon atoms are eliminated as a consequence. Two of the existing analyses strongly imply that the structure may contain hydroxyl ions at particular sites in the structure. Nevertheless, it seems highly probable that groups of tetrahedral hydroxyls occur also, because of the inadequacies in silicon and carbon when compared with the material from Scawt Hill.

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Added in press. The very recent work of R. E. Moore and Wilhelm Eitel (*Naturwiss.* **44,** 259 (1957)) discusses a borosilicate of the apatite group and raises the question of the coordination number of the boron, i.e. whether the structure contains (BO_3) or (BO_4) or both. Although Gruner and McConnell (*Zeits. Krist.* **97A,** 208–215 (1937)) considered the occurrence of (CO_4) in francolite, the slight displacement of the three oxygens necessary to produce 4(CO_3) rather than 3(CO_4) seems more probable and more closely fits the chemical calculations.

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THE CHEMICAL ANALYSIS OF IRIDOSMINES AND OTHER PLATINUM-METAL MINERALS

A. D. Westland and F. E. Beamish, *University of Toronto, Toronto, Ontario, Canada.*

Abstract

Some of the difficulties associated with the chemical separation and determination of the constituents of iridosmines are discussed and the methods of dissolution are reviewed. Applications of these procedures to the analysis of iridosmines from various world sources are made and the conclusion is reached that significant and hitherto unsuspected mineralogical data can be obtained by the use of accurate chemical analysis of micro crystals whose composition may differ considerably from that of the accumulation of crystals from a single deposit. These micro methods of analysis have revealed the presence of palladium in iridosmines; and the existence of minerals with higher and lower osmium contents than any hitherto reported.

Introduction

Platinum, palladium, rhodium, iridium and osmium have been known for over 150 years and the sixth element of the family, ruthenium, for 112 years. These metals have been used commercially for much of this time but in spite of this fairly long history, the mineralogy of this group is relatively little known. The compounds, cooperite, PtS; braggite, (Pt, Pd, Ni)S; laurite RuS_2; sperrylite, PtAs; potarite, PdHg; and stibiopalladinite, Pd_3Sb; have been reported, but it is asserted that the occurrences of the platinum metals consist chiefly of native metals or alloys of the precious metals containing small amounts of iron, nickel, copper, etc. This judgement is directed by the fact that the precious metals have been frequently discovered in, and obtained commercially from, deposits containing fairly large metallic grains, However, in many deposits, e.g. the sulphide nickel ore of the Sudbury district in Ontario, the bulk of the platinum is too finely dispersed to allow easily the determination of its mineralogical form. It may occur as free metal, as a compound with a non-metal or base metal, or even as a substitute for a base metal in a mineral of the latter. Free metal is suggested as the principal form in the Transvaal sulphide ores. At least some "compounded" platinum is present in the Ontario ores for it was in these that sperrylite was first discovered. It has been recorded that in these deposits, palladium may be present as a selenide. The third type of occurrence, suggested above, may be represented by the Bolivian penroseite studied by Herzenberg (1). This, a complex selenide, was found to contain appreciable amounts of platinum and palladium in addition to the usual base metals. It seems that some information could be obtained concerning these occurrences by an examination of single grains of the ore constituents. Indeed, such a microscopic investigation was made of the sulphide ore of Norilsk, Russia (2). It revealed three types of grains which were probably precious metals minerals. Of a number of grains isolated, forty-three resembled cuprite but were not identified. Twenty-one appeared to be platinum-palladium alloy, and four were believed to be sperrylite. Obviously, micro-analytical methods applied in these instances would have given pertinent information.

An example of the paucity of information on platinum occurrences is presented by the mineral niggliite. Only one small grain of this has been reported, and the detection of tellurium and a platinum analysis indicated the formula $PtTe_3$ (3). On the basis of the indexing of the x-ray diffraction pattern and a comparison of its properties with those of analogous compounds, Meijer preferred the formula PtTe (4). Although the authors have no information concerning the method of analysis it is a fact that when tellurium is separated as metal, much of the platinum is lost by coprecipitation.

Concerning the mode of appearance of platinum in natural deposits, little has been recorded concerning the possibility of silicate-platinum combinations. Even though it is generally accepted that platinum metals occur almost exclusively in basic and ultra basic rocks, there is some evidence that silicates may be formed. In the authors' researches there have been data accumulated which point almost indisputably to the union of ruthenium or osmium with silica; in the latter case to form residues from which osmium could not be volatilized even at red heat. With ruthenium the incorporation of silica resulted in a residue which resisted the usual treatment and a special technique was required for its separation from the remaining platinum metals. Other researchers have noted the association of ruthenium and silica. Thus Zvyangintsev (5), who provided a more detailed description of his work than one usually encounters, observed silica as a residue subsequent to removal of ruthenium. From these observations it would seem that one should not discount the existence of naturally occurring silicates of the platinum metals.

The principal obstacle in the determination of compositions of these minerals is the difficulty of chemical analysis, especially of minute grains. Only recently have accurate micro analytical methods for individual platinum group metals become available and restricted separation schemes are now appearing in the literature (6, 7, 8).

The minerals of the platinum metals other than those alloys which are composed almost entirely of noble metals, are exceedingly rare. There has been much study of native platinum and a fairly large number of compositions have been recorded. Rather less attention has been given to iridosmine, the next most important mineral. The older reports of analyses of iridosmine and native platinum are characterized in most cases by an absence of detailed procedure, of reference to inherent analytical difficulties, and of any estimate of accuracy or even precision. The result has been an unreasonable acceptance and perpetuation of unreliable mineral compositions. The difficulties in these analyses are not merely matters of technique; a search of the literature reveals no comprehensive procedure which has been proved valid by either its application to synthetic standards or by the use of some method of comparison. It is partly this situation which introduces a serious element of doubt concerning the meaning and validity of many published compositions of native platinum minerals, particularly of iridosmine. Concerning the latter there seems to have been little appreciation of its identity. Thus, for example, in the analysis of native platinum quoted by Hintze (9), the quantities of the constituents are reported in percentages of platinum, palladium, rhodium, iridium, osmiridium, and some base metals. Osmiridium, or iridosmine is, however, a composite material. Therefore, reports of this kind do not reveal the more significant elementary composition. This neglect would not be particularly significant if the proportions of the iridosmine or "insoluble matter" were very small, but it has been reported present in amounts up to 22.5% in California, 26.0% in Australian, and 37.30% in Oregon platinum. These figures are in contrast to reported iridium contents of only 4.29%, 2.20, and 0.40% respectively.

In view of the above situation, it may be useful to review critically the state of the analytical chemistry of the precious metal minerals and to present a few data on mineral compositions obtained by using a method developed in this laboratory. Since the source of the difficulties in the analysis of platiniferous materials is exemplified in the analysis of iridosmine, this mineral will be considered in some detail.

The Iridosmine Series

"Iridosmine" is a name used to denote the members of a series of metallic minerals of the platinum group among which the composition may vary widely. The chief components are iridium, osmium, and ruthenium. Small amounts of base metals as well as the remaining platinum group elements are usually, if not always, present. A considerable quantity of gold has been found in some specimens (10). Orginally the investigations of iridosmine resulted in the discoveries of iridium, osmium, and ruthenium and this mineral has remained the principal source of these metals. It was first recognized in the year 1805 (11) and was obtained as a residue upon dissolving crude platinum in aqua regia.

These iridium alloys are frequently very hard, non-malleable, and extremely resistant to chemical attack, especially in the massive state. They are often more resistant than any of the component metals individually, and this property combined with the impracticability of grinding them accounts further for some of the analytical difficulties.

Dissolution and Analytical Methods

The first analyses were carried out by Rose (12) and Berzelius (13) but as ruthenium, which is invariably present, had yet to be discovered, the analyses must be regarded as suspect. Subsequent to this work Claus discovered ruthenium (14), and published some analytical data (15).

Of the analyses which are reported in mineralogy treatises, e.g. Dana's (16), the majority were made about one hundred years ago (17). For these, like those of the earlier period, large quantities of fairly finely divided material were used and being in such a form, responded to the attack of a nitrate fusion. Although the older literature is far from explicit, it is to be expected that the dissolution was not complete, for it fails when applied to large grains.

The first major contribution to the special techniques for the analysis of iridosmine resulted from the work of Deville, Debray, and Morin (18). They found that iridosmine could be alloyed directly with zinc, and the latter volatilized leaving the metal in the form of a very finely powdered zinc alloy. Subsequent leaching with acid removed most of the zinc. The resulting powder was largely susceptible to a barium nitrate fusion. This method, intended for the preparation of more than twenty-five kilograms of iridium, was subsequently adapted by Leidé and Quennessen to the analysis of samples weighing about ten grams (19). These authors substituted sodium peroxide for the nitrate in the oxidizing fusion. The mineral, previously pulverized by fusing with zinc, was mixed with 40 g. of sodium peroxide and the mixture added in small portions to 10 g. of molten sodium hydroxide contained in a nickel crucible. The melt was maintained at a bright heat for 30 minutes after which time it was cooled and taken up in a liter of water. Insoluble matter was separated by filtration, washed with sodium hypochlorite, and dissolved in hydrochloric acid.

In order to prevent air oxidation and consequent volatilization of osmium, the zinc fusion was made under a slag, for which alkali chlorides or zinc chloride were used. In a recent publication (20) this oxidation was used to remove most of the osmium which was subsequently condensed. Bearing in mind that there would be only a partial separation of osmium, there would seem to be unnecessary complications.

These zinc and perioxide fusions have become standard procedures for the attack of irodosmine or the "insolubles" that appear in the course of ore assays. The procedure was accepted by Schubin (21) and Gilchrist (22). Despite its general use the method cannot be considered entirely satisfactory, particularly for the analysis of small samples. Considerable quantities of foreign metals are generally introduced; nickel, iron, gold, or silver from the crucible; sodium or barium from the caustic flux; zinc, and possibly lead and other metals from the alloying fusion. Of even greater concern, is the fact that the attack must be repeated, often several times, to effect dissolution and fails even then to corrode the more resistant alloys. Zvyangintsev (23) indicated what may have been the earlier accepted practice, namely to repeat the caustic fusion until the operator became weary of it and then to discard the still unattacked residue, subtracting its weight from that of the initial sample.

Not only may the process of dissolving be incomplete, but it has been the experience in this laboratory that with certain minerals there may be no evidence of any corrosion. Thus Hill and Beamish were unable to dissolve a sample of Tasmanian iridosmine by these traditional methods (24).

The inefficiency of the classical fusions was recognized by the National Bureau of Standards in Washington. A new approach to the problem was undertaken and led to a much improved procedure (25, 26). By this method platinum metals and their alloys are converted to soluble chlorides by heating to 300° C. in a closed Pyrex tube containing hydrochloric acid and an oxidant such as sodium chlorate. Following the reaction, the tube is opened under a solution of 1:1 hydrochloric acid saturated with sulphur dioxide and appropriate separations and determinations carried out. This method, or modifications of it, is now used by some of the larger platinum metals producers.

In practically all cases attack is complete, but Hill and Beamish found as before that Tasmanian iridosmine resisted quantitative corrosion. It may be that considerable quantities of ruthenium may result in incomplete attack, for this metal exhibits considerable resistance.

In order to ensure complete dissolution of iridosmines Hill and Beamish used chlorine gas at 680–720° C. for the oxidation of microsamples (24). Although the process is an old one no record exists of its successful application to quantitative work. The alloy must be covered with sodium chloride in order to avoid the formation of an inert clinker in the sample boat. Again, the minute grains of the native alloys were not analyzed by Hill and Beamish, there being available at that time no dependable scheme for the analysis of micro amounts of the platinum metals. However, they found that the chlorination procedure could be used for the quantitative dissolving of iridosmines and was more generally dependable than the sealed tube method and more convenient in manipulation.

Although the boat residues from chlorinations of iridosmine were entirely soluble and presumably could be analyzed by any valid procedure, there was no justification for assuming that the sublimates and gases that formed could be recovered quantitatively in convenient form, i.e. in aqueous solution, and analyzed. In fact, two major difficulties appeared. Ruthenium and platinum chlorides sublimed and condensed on hot surfaces of the reaction tube to form insoluble crystalline modifications (27, 28); and osmium was difficult to recover, since, in the presence of oxidizing agents, it was converted to the volatile tetroxide. However, as indicated below, these difficulties were overcome.

SEPARATION AND DETERMINATION OF THE MINERAL CONSTITUENTS

It is certain that early mineral analyses were carried out on large samples, from which it was relatively easy to recover the constituents quantitatively with, no doubt, some cancellation of errors within the multiplicity of procedures. Unfortunately the records of the compositions of minerals determined by the traditional methods bear no evidence that separations were complete and that isolated constituents were pure. The fact that the totality of the latter was close to one hundred per cent is unacceptable as evidence of accuracy. The device of obtaining the more insoluble platinum metals by difference discourages confidence in the reported values. Where the amount of insoluble was neglected the values are increasingly suspect.

There is then little doubt that some of the early methods of separating the platinum metals were significantly inefficient. Much use was made of ammonium chloride as a precipitant for iridium and platinum. For various reasons this process does not provide acceptable accuracy and at the same time persistently clean separations even upon continued reprecipitation (29). A second procedure used originally, and still so used, for the separation of rhodium and iridium, has been applied analytically. In this method separation is effected by selectively leaching a pyrosulphate melt of the metals, to dissolve rhodium. Such selective dissolutions are seldom if ever to be recommended for precise analytical work. In the past osmium and ruthenium have almost always been separated by distillation from oxidizing media. Although this principle is still accepted as by far the best, the early procedures required improvement.

Apart from the separations, the determinations were not refined until well into the present century. Thus, for example, Leidé and Quennessan (19) collected osmium in sodium hydroxide solution and precipitated it subsequently on aluminium strips. The same authors collected ruthenium in hydrochloric acid, evaporated to dryness, and after taking up the residue in water, precipitated the ruthenium from solution with magnesium strips. Iridium was also precipitated from the distillation residue by magnesium. Such precipitates were leached with acid to remove the base metal. Thus, it is not surprising that Leidé and Quennessen failed to find platinum, palladium and rhodium in their mineral samples. It is significant that no further samples of iridosmine have been reported free of all of these elements. Osmium was generally determined by distillation into caustic solutions and precipitation by neutralization with acid. This method was shown by Gilchrist to be inaccurate because of the inevitable contamination by alkali (30). Ruthenium distilled and collected in hydrochloric acid was, and often still is, determined by simply evaporating to dryness, reducing the residue in hydrogen, and weighing. Such procedures may suffice for large quantities, but have not proved efficient for milligram amounts.

Because of the general failure to present data in support of procedures, one has the impression that before the Bureau of Standards initiated its program of platinum metals research, the analysis of platiniferous materials depended largely on methods sanctioned only by tradition, few of which had been subjected to critical examination.

In a series of publications, Gilchrist provided schemes of separation and analysis which will probably long remain standard procedures for macro amounts of the platinum metals (31). It was only upon the appearance of these that it became possible to analyze accurately solutions of mixed platinum metals.

However, a great many precious metals assays and associated analyses are concerned with much smaller amounts than those dealt with by Gilchrist. The analysis of small grains of minerals or of the "insoluble" from fire assay methods involves amounts of the order of micrograms.

In the course of twenty-five years of study in the authors' laboratory, micro-procedures for all of the noble metals have been developed. It has been shown that many of the "macro procedures" do not provide accurate results for micro separations and determinations. Micro methods such as the colorimetric, have been appearing for some time but methods of separation are still neglected. Of the latter, some very promising procedures, notably the chromatographic separation of Pt, Pd, Rh, Ir, and base metals (7), have been published, but evidently there has been no integration of these procedures to produce a comprehensive scheme of analysis. Obviously such procedures can not be applied directly to mineral analysis although a number are capable of application to fire-assay buttons or cupellation beads (32, 33, 6, 34, 35).

The authors have also devised a comprehensive scheme of micro analytical separations for the six platinum elements and have succeeded in developing a procedure for the complete dissolution of platinum metals by the dry chlorination method (8, 36). These publications include verification of the procedures using synthetic solutions and pure metals, and the methods were subsequently applied in the analysis of natural alloys. Some account of this work is included below.

Analysis of Milligram Amounts of Iridosmine Minerals

The difficulties encountered in the dry chlorination of osmium, ruthenium, and platinum, have been overcome. It has been demonstrated that micro amounts of these metals may be converted quantitatively to soluble products and subsequently determined (36). To accomplish quantitative corrosion, the sample was placed in a small Vycor glass tube and covered with sodium chloride. The inside of the tube had to be prepared previously by coating with fused sodium chloride over the regions located at the ends of the hot zone. The tube containing the sample was heated to a temperature of about 700° C., while a slow stream of chlorine was passed through it. The exit gases were led into a train of four receivers containing in the case of the first, sulphurous acid, and thereafter, 6 normal hydrochloric acid, kept saturated with sulphur dioxide by an excess of the gas led into the first receiver. After evaporating the hydrochloric acid solutions to give a few ml. volume, they were combined and analyzed.

The analysis of complex systems follows the course of the analytical scheme published previously (8). The presence of base metals introduces a considerable difficulty. Two approaches to the problem of separation of these may be applied subsequent to the removal of osmium and ruthenium in which process the presence of base metals is not objectionable. The well-known method of Leidé (37) for separating base metal hydroxides from the platinum group is normally quite effective. The separation would be uncertain for small quantities, however, unless a carrier were added to increase the bulk of the hydroxide precipitate. Another disadvantage is the use of nitrous acid which it is desirable to avoid because of the difficulty of destroying the complexes which it forms.

A new approach which promises to be of great value is separation by ion exchange. The principle involves the tendency for base metals to form cations, and the ease of the formation of platinum metals anions. Coburn, et al. (38) have shown that large quantities of iron, copper and nickel may be separated from palladium and platinum by an ion exchange resin. Fraser (39) had thus previously separated small amounts of base metals from palladium. Of the platinum group, palladium is the most similar to the base metals so it seemed probable that the base metals could equally well be separated from rhodium and iridium using the same conditions. Work now in progress has proved this assumption. The authors have shown in a previous publication that nickel may be separated from iridium (40). Although it was not extensively tested, the following procedure for the removal of base metals was found satisfactory.

The sulphuric acid residue from the distillation of ruthenium was transferred to a 50 ml. beaker and evaporated on a steam bath and a "medium" hot plate to about 1 ml. volume. The sample was diluted with a little water, 5 ml. concentrated hydrochloric acid were added, and the sample was boiled for 0.5 hour, adding more hydrochloric acid when necessary. The sample was boiled finally to 3 ml. volume, 1.5 g. sodium chloride were added and the solution was diluted to about 30 ml. volume. The solution was passed through a column of Dowex 50 ion-exchange resin and the effluent was evaporated to about 20 ml. volume and the separation and determination of palladium, etc. carried out as described previously (8). Most of the sodium was retained by the resin. The column was eluted with 2 normal hydrochloric acid and qualitative tests for iron and nickel applied to the eluates. Iron was precipitated as hydroxide and nickel was detected by means of dimethylglyoxime. These procedures were applied in analyses of iridosmine and other precious metal minerals, and some of the results are recorded in Tables I and II. Samples 1–3 were "iridosmine" of unknown source, No. 4 was a "Tasmanian iridosmine." Samples 5 and 7 were supplied by Harvard University, Department of Mineralogy and labelled "Iridosmine and Osmium" from Colombia. No. 6 was obtained from the American Museum of Natural History and was labelled "Iridosmine form Nizhne Tagilsk, Urals. No. 8 was obtained from the Smithsonian Institution, Washington and was labelled "Iridosmine, var. nevy-anskite, Nevyansk, Urals." An account of the physical examination of these minerals follows:—

Single grains were split or broken into two or more pieces. One of the pieces was examined for the presence of base metals with the aid of a Hilger medium quartz spectrograph with an arc source. Many lines not attributable to the platinum metals appeared in each case, and some of these were identified. In the cases where clear hexagonal habit was not evident, the samples were examined by x-ray diffraction. The structure of No. 6 was not apparent from microscopic examination but it could not be crushed or ground so that an x-ray powder pattern was not available. Other pieces of each mineral were analyzed quantitatively. In several cases the grains contained silica in cracks or between lamina.

Table I. Base Metal Composition of Iridosmines

No.	Crystal symmetry	Locality	Base metals present
1	Hexagonal	Unknown	Not examined
2			
3			
4	Hexagonal	Tasmania	Cu, Ag, Pb.
5	Hexagonal	Colombia	Cu, Sn, Pb, Fe*
6	?	Nizhne Tagilsk, Urals	Ag, Sn, Pb, Fe, Cu, Co
7	Cubic	Colombia	Ag, Sn, Pb, Fe*, Cu, Ni*
8	Hexagonal	Nevyansk, Urals	———

* Detected by wet chemical methods.

This was removed by scraping with a needle and in some cases by leaching with hydrofluoric acid. The results of the qualitative examination appear in Table I.

Two parts of the one grain were used in the analyses of Nos. 2 and 3 (Table II). The mineral possessed a lamellar structure, individual plates of which could be split apart with a steel needle. Sample No. 1 was a different grain obtained from the same deposit.

The samples were weighed on a Sartorius micro-balance and were chlorinated for at least 10 hours. Close examination of the solutions obtained upon dissolving the chlorination products failed to reveal the presence of insoluble matter and it was concluded that dissolution was complete. The platinum metals compositions are given in Table II.

Several points of interest are apparent from the investigations. It can be seen that two crystals (samples 1 and 3) from the same locality can differ widely in composition. Fairly good precision was obtained by analysing two portions of the same crystal for ruthenium (samples 2 and 3). This points out the possible lack of significance of existing published data obtained from large composite samples of iridosmine.

Table II. Analysis of Iridosmine Samples

No.*	Weight of sample, mg.	Osmium		Ruthenium		Palladium		Platinum		Rhodium		Iridium	
		μg.	%	μg.	%	μg.	%	μg.	%	μg	%	μg.	%
1	1.570	600	38.2	5.0	0.32								
2	3.129	1360	43.5	398	12.7								
3	3.924	—	—	475	12.1								
4	0.267	139	52.1	7.0	2.6	3.2	1.2	14	5.3	8.4	3.1		
5	2.921	1210	41.1	442	15.1	13.4	0.5	16	0.6	40.8	1.4	905	31.0
6	1.253	395	31.5	223	17.8	8.5	0.7	47.4	3.8	39.0	3.1	345	27.6
7	1.459	173	11.9	40.5	2.8	8.6	0.6	165	11.3	86.4	5.9	814	65.8
8	1.420	1320	93.0	50.5	3.6	5.2	0.4	10	0.7	8.9	0.6	100.5	7.1

* The sample numbers correspond to those in Table I.

Hitherto palladium has not been reported as a constituent of iridosmine. Since the procedure for palladium used in the present work is much more sensitive than any hitherto employed, it was possible not only to detect but to determine minute amounts of this metal in the minerals.

Zvyagintsev (41) has suggested that iridium-osmium alloys containing less than 31% osmium possess a face-centred cubic lattice. Sample No. 7 possessed a very low osmium content (11.9%) and *x*-ray diffraction showed it to have a cubic lattice. The lattice cell dimension of iridosmines were reported by Zvyagintsev (5) to vary but slightly with changes in composition and the axial ratio to vary not at all. No marked deviations of the lattice constant from that of pure osmium were observed by the authors among hexagonal iridosmines. Larger differences were observed for the cubic structures but these were still small. This lack of response of the lattice constants to changes in composition is due presumably to the similarity in size of the metallic radii of all six platinum metals.

Thirty-one analyses of Tasmanian iridosmine were reported by Nye (42). Two samples of the Tasmanian mineral were available to the author. Both consisted of very small crystals each weighing about 5 micrograms. By examining the samples under a microscope it was possible to see two and possibly three types of crystals. The most abundant type was the usual tabular hexagonal form; a fairly rare one was long and lathe-like; a third was similar to the nuggets characteristic of native platinum. *X*-ray diffraction revealed the presence of both hexagonal and cubic modifications.

Several dozen of the hexagonal variety were separated by picking them up with a needle wetted with alcohol. A one-quarter milligram sample was prepared in this way. The osmium value found by the author (52.1%) is higher than the average reported by Nye (viz. 45.5%). It is possible that Nye's samples were poorer in osmium due to the presence of cubic (low osmium) constituents, but in view of the variations that can occur among crystals taken from one locality, this explanation may be invalid.

Sample No. 8 was of particular interest. It was in the form of a well defined warped hexagon a little larger than a pin head. A corner of the hexagon was broken off for the analysis and in this process it was observed that the alloy was much more malleable than the other iridosmines and did not "cry" when bent. The bulk of the crystal was placed on a carbon electrode and exposed to the arc for one minute. Unlike all the other minerals examined, it did not melt and yielded only a very faint spectrum from which no evidence of minor constituents was obtained. The crystal was heated to redness in air for a five minute period.

Microscopic examination revealed no apparent change in the crystal other than a darkening of the colour and decrease in the lustre. However, when the crystal was then touched with a needle, it broke very easily and the freshly exposed surfaces were quite black. The osmium probably had been volatilized. Surprisingly the geometric structure was retained upon ignition; it was expected that only a small black residue would remain, considering its high osmium content. Although this sample was labelled "Iridosmine, var. Nevyanskite," it contained more osmium than any sample hitherto reported and more than that allowed by the definition in Dana's System of Mineralogy (16). Actually the amount of osmium present was so great that it was in excess of the optimum amount for the determination. Consequently the total composition reported is somewhat high. It would seem that either the definition should be extended to include minerals possessing a greater osmium content, or else the present sample should be regarded as a native osmium, a mineral category not yet established. In this connection it may be noted that sample No. 7 contained less osmium than any sample previously reported.

In view of the fact that these osmium-iridium alloys may have such varied compositions that two crystal structures are permitted, the designation of all such minerals by the name "iridosmine" seems inadvisable.

It must be emphasized that with milligram samples, results as accurate as those obtainable with macro amounts are not to be expected. Most of the procedures described above are recommended only for micro samples. It is therefore suggested that for maximum accuracy, and where sufficient material is available, a sample of the mineral weighing at least a few tenths of a gram should be started with one of the older procedures and the insoluble material then chlorinated, using the present procedure. The products of the two treatments could be combined, and analyzed by the methods described by Gilchrist.

It should be noted also that in the micro scheme, the determination of iridium is the most difficult of all of the platinum metals determinations. This is partly due to the absence of suitable methods and partly because the determination is made at the conclusion of a long series of difficult operations. It would be highly desirable to have an independent method for the direct determination of iridium, or one which could be applied after the determination of osmium and ruthenium.

SUMMARY

Metallic precious metals minerals may be quantitatively attacked by chlorine to obtain salts soluble in aqueous media.

Composite samples of iridosmine should be separated by hand from admixed substances and since such samples are small, they must be analyzed by micro procedures. These procedures are also recommended for the analysis of insoluble material occurring frequently in macro analyses and ore assays.

Analyses of a variety of iridosmine minerals were carried out on the micro scale. It is shown that crystals of iridosmine from the same source can differ widely in composition, but uniformity of composition in a single grain may be expected.

Palladium appears to occur generally in iridosmine in minute amounts.

Since the occurrence of cubic structures in iridium-osmium minerals has been confirmed, the inclusive designation of these minerals by the name "iridosmine" seems inadvisable. The discovery of a mineral containing such a high percentage of osmium that it may well be called "native osmium," also suggests a reconsideration of the nomenclature of the precious metals minerals.

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THE CRYSTAL STRUCTURE OF SANBORNITE, $BaSi_2O_5$

ROBERT M. DOUGLASS, *Department of Geological Sciences, University of California, Berkeley 4, California.**

ABSTRACT

Sanbornite, previously described as triclinic, is orthorhombic, space group *Pcmn*. The unit cell, $a_0=4.63$, $b_0=7.69$, $c_0=13.53$ Å, contains 4 $BaSi_2O_5$.

A structure with thirteen parameters has been found, yielding an overall residual factor R of 0.10. It is a silicate sheet structure with two $(Si_4O_{10})^{-4}$ sheets per unit cell lying parallel to (001) at $z=1/4$ and $3/4$, and two barium ions lying roughly half way between each successive pair of sheets. Each sheet consists of continuously linked, distorted, six-membered rings of SiO_4 tetrahedra. Unshared vertices of tetrahedra lie on both sides of each sheet. Each barium ion is surrounded by seven near oxygen ions. Interionic distances are of expected magnitude.

INTRODUCTION

The mineral sanbornite, $BaSi_2O_5$, was first described by Rogers (1932). Only one occurrence is known, near Incline, Mariposa County, California,† where it is found with the rare mineral gillespite ($BaFeSi_4O_{10}$; known from only one other locality), quartz, witherite and other minerals. Sanbornite occurs as white to colorless, translucent to transparent, anhedral plates up to 2 or 3 cm. across and up to 5 mm. in thickness. Cleavage parallel to (001) is very prominent, and the cleavage lamellae are brittle and exhibit a pearly luster. Cleavage parallel to (100) is very much less prominent and cleavage parallel to (010) is indistinct.

Many fragments of sanbornite when examined between crossed polarizers show an extinction effect which Rogers interpreted as polysynthetic twinning on (010) [(100) of the present paper] with small, variable extinction angles to the trace of this plane. On this basis, lacking morphological or *x*-ray evidence, Rogers assigned sanbornite to the triclinic system. Rogers noted, however, that "the twinning is not as sharp and well defined as the usual albite twinning of plagioclase. The plates are usually somewhat bent and distorted, so much so that the angle between (001) and twinned ($\underline{001}$) could not be determined with the reflection goniometer." The crystals selected for the present single-crystal *x*-ray examination showed no optical or *x*-ray evidence of twinning. The *x*-ray diffraction symmetry of sanbornite is orthorhombic, indicated by intensity relationships as well as metrically.

Platy crystals of $BaSi_2O_5$ obtained from melts were first described by

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* Present address: University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

† Three small veins, from a few inches to a few feet in width, in metasediment, about 1500 feet N. 15° W. of Trumbull Peak, NE. 1/4 Sec. 9, T. 3 S., R. 19 E., Mount Diablo base and meridian, close to 4400 feet in elevation.

Bowen (1918) as orthorhombic. Eskola (1922) also obtained $BaSi_2O_5$ crystals from melts and again believed them to be orthorhombic. To reconcile his findings with those of Bowen and Eskola, Rogers postulated dimorphism of $BaSi_2O_5$, but this has not been substantiated. In the present study sanbornite, sanbornite heated to just below the melting point*, and a sintered mixture of the composition $BaSi_2O_5$ or "$BaO \cdot 2SiO_2$" ($BaCO_3+2SiO_2 \cdot xH_2O$ heated at 1450° C. for $1\frac{1}{4}$ hours and at 1375° C. for $2\frac{3}{4}$ hours) gave the same x-ray powder diffraction pattern. This pattern is compared in Table 1 with d spacings calculated from cell dimensions obtained from single-crystal photographs, and with uninterpreted patterns for "$BaO \cdot 2SiO_2$" given by Austin (1947) and Thomas (1950), the latter reporting "only the most persistent peaks". An uninterpreted powder pattern for "$BaO \cdot 2SiO_2$" given by Levin and Ugrinic (1953) contains many lines for which there are no corresponding calculated spacings and is otherwise in serious disagreement with the above three patterns, so that comparison of this pattern with the others is not feasible. It seems clear that in the material of Levin and Ugrinic the preponderant phase was not $BaSi_2O_5$ of sanbornite structure.

Optical data for $BaSi_2O_5$ as reported by various investigators are summarized in Table 2.

CELL DIMENSIONS AND SPACE GROUP

Weissenberg and precession photographs obtained from several single crystals of sanbornite using

$$\text{Cu} \quad (K\alpha_1 = 1.54050 \text{ Å.}, K\alpha_2 = 1.54434, K\beta_1 = 1.39217)$$

and

$$\text{Mo} \quad (K\alpha_1 = 0.70926, K\alpha_2 = 0.71354, K\beta_1 = 0.63225)$$

radiation showed Laue symmetry *mmm* and gave cell dimensions $a_0=4.63\pm0.01$ Å, $b_0=7.69\pm0.02$ Å, $c_0=13.53\pm0.02$ Å; cell volume 482 Å^3; $a:b:c=0.602:1:1.759$. (The convention $c<a<b$ is not followed here for the sake of emphasizing the structural relation of sanbornite to other sheet silicates.) Systematic absences were found only for diffraction maxima with l odd in $0kl$ and with $(h+k)$ odd in $hk0$. Diffraction symbol $mmmPc\text{-}n$ is thus indicated, embracing space groups $Pcmn$ (D_{2h}^{16}) and $Pc2_1n$ (C_{2v}^{9}).

In the hope of deciding between these two space groups, evidence for absence of a center of symmetry was sought by testing for a piezoelectric effect. No piezoelectric effect was detected with an adaptation of the Stokes (1947) modification of the Giebe-Scheibe apparatus. Crystal

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* The melting point of $BaSi_2O_5$ has been reported as 1420° C. (Eskola, 1922) and 1418° C. (Levin and Ugrinic, 1953).

TABLE 1. POWDER *X*-RAY DIFFRACTION PATTERNS FOR $BaSi_2O_5$

Calculated			Measured		Austin (1947)[4]		Thomas (1950)[5]	
hkl	*d*, Å	*I*[1]	*d*, Å[2]	*I*[3]	*d*, Å	*I*	*d*, Å	*I*
002	6.77	18.9	6.79	30	6.7	9		
012	5.08	20.5	5.08	30				
101	4.38	0.1	—	—				
110	3.97	95.8	3.97	100	4.00	100 (1)	3.98	VS
020	3.84	4.1 } 10.5	3.82	10				
102	3.82	1.1						
111	3.81	5.3						
112	3.422	47.0 } 49.9	3.422	50	3.55	20		
004	3.382	2.9						
022	3.342	60.0	3.342	70	3.28	23	3.35	M
103	3.231	18.3	3.226	20				
014	3.096	50.6	3.092	75	3.14	60 (2)	3.12	S
113	2.979	4.6	2.980	5				
121	2.890	3.7	2.888	5				
104	2.731	22.5 } 67.4	2.720	55	2.77	36	2.72	W
122	2.710	44.9						
114	2.574	13.0	2.574	15	2.60	10		
024	2.540	3.3	2.541	5				
123	2.473	0.0	—	—				
032	2.397	5.2	2.394	5				
105	2.336	2.7	2.327	5				
200	2.315	13.0	2.317	15	2.35	22		
201	2.282	1.4	2.281	<5				
006	2.255	0.0	—	—				
130	2.243	8.7 } 8.8	2.236	10				
115	2.235	0.1						
124	2.227	31.0	2.226	30	2.27	50 (3)	2.23	W
131	2.212	0.3	—	—				
202	2.190	11.4 } 15.4	2.193	15	2.23	50		
211	2.188	4.0						
016	2.164	18.7	2.162	25	2.17	50		
132	2.129	47.2	2.130	40	2.06	25	2.13	W
212	2.107	12.0	2.109	10				
203	2.060	1.6	—	—				
034	2.043	6.8	2.038	5				
106	2.027	13.1	2.025	15				
133	2.008	0.6	—	—				
125	1.997	2.9 } 12.8	1.990	10				
213	1.989	6.4						
220	1.983	3.5						
221	1.962	0.0	—	—				
116	1.960	0.0	—	—				
026	1.945	0.0	—	—				
040	1.922	12.2	1.921	10	1.91	15		
204	1.910	1.9	—	—				
222	1.903	14.6	1.903	10				
134	1.869	1.7	—	—				
214	1.854	14.1 } 20.9	1.850	20	1.87	20		
042	1.849	6.8						
223	1.815	3.0	1.815	5				
126	1.793	20.7	1.793	20	1.78	12		
			1.736	5				
			1.709	5				
			1.690	15				
			(About 50 more lines observed)		1.59	10		
					1.48	13		
					1.46	10		
					1.29	10		

[1] Relative intensities calculated for Cu Kα radiation ($\lambda = 1.5418$ Å).

[2] Philips 114.6 mm. diameter powder camera, Straumanis mounting; 0.2 mm. diameter glass capillary with walls 0.1 mm. thick, containing mixture 50 per cent by volume each of sanbornite and powdered silica glass (to minimize the otherwise serious preferred orientation in the powder sample, arising from the prominent {001} cleavage); Cu Kα radiation.

[3] Relative peak intensities above background from densitometer measurements of powder photograph on Eastman Kodak Type *AA* film for which density was calibrated as a function of exposure time.

[4] $BaO \cdot 2SiO_2$ mixture fired twice to maximum temperature of 1430° C. and crystallized at 1400° C.; duplicate patterns obtained from two different samples, "checked petrographically and found to be homogeneous," with a Philips diffractometer using "copper K alpha radiation, filtered by nickel." Numbers in parentheses in *I* column indicate the three strongest maxima as noted by Austin.

[5] Thomas reported "only the most persistent peaks" summarized from several patterns obtained with a Philips diffractometer using "Cu Kα ($\lambda = 1.5393$ a. u.) radiation with a nickel filter."

TABLE 2. OPTICAL DATA FOR $BaSi_2O_5$

Eskola (1922)	$BaSi_2O_5$	—	—	$\gamma \perp$ prominent cleavage
Rogers (1932)	Sanbornite	$\alpha \approx b$	$\beta \approx a$	$\gamma \approx c$ ($\backsim\perp$ prominent cleavage)
This paper	Sanbornite	α-a	β-b	$\gamma = c$ ($\perp$ prominent cleavage)

		α	β	γ	$2V_\alpha$	$(\alpha \cdot \beta \cdot \gamma)^{1/3}$
Bowen (1918)	$BaSi_2O_5$	(*1*) 1.595	1.613	(*3*)	~70° (meas.)	—
		(*2*) 1.598	1.617			—
Eskola (1922) (5893 Å)	$BaSi_2O_5$	1.597	1.612	1.621	~75° (meas.)	1.610
					75° (calc.)	
Rogers (1932)	Sanbornite	1.597	1.616	1.624	65° (calc.)	1.612
Greene and Morgan (1941)	$BaSi_2O_5$	1.598	1.619	—	—	—
This paper (5893 Å)	Sanbornite	1.598	1.617	1.625	67° [meas. (*4*)]	1.613
		±0.001	±0.002	±0.002	65° (calc.)	

Mean refractive index calculated for $BaSi_2O_5$ [using density 3.77 g. cm.$^{-3}$ calculated from sanbornite cell dimensions and specific refractive energies from Larsen and Berman (1934)] 1.610

Lorentz-Lorenz refraction .... 25.3 cm.

(*1*) Crystals in barium-rich glass.

(*2*) "Pure" crystals from $BaSi_2O_5$ melt.

(*3*) Bowen reported refractive indices for the two vibration directions parallel to the platy development of his crystals as α and γ, the optic axial plane thus lying parallel to the plates (see his Fig. 2). He did not report a value for β presumably because of the thinness (ca. 0.03 mm.) of his plates, although he did report an optic axial angle. It seems apparent, however, that Bowen's α and γ are to be correlated with α and β, respectively, of the above table, in which case the optic axial plane must lie normal to Bowen's plates rather than parallel to them, and his crystals are platy parallel to (001).

(*4*) Measured with the universal stage and by the Mallard method.

fragments suspended on fine nylon filaments and dipped into liquid nitrogen exhibited on removal from the liquid nitrogen no electrostatic charge. The absence of positive indication of a piezoelectric effect or combined pyro-piezoelectric effect and the lack of morphological data preclude a choice between the two possible space groups at this stage.

DENSITY, COMPOSITION AND CELL CONTENT

A sample of sanbornite for analysis was purified as follows: The rock was crushed to pass 60 mesh and washed with bromoform (G. = 2.88) to remove light minerals (principally quartz). Gillespite ($BaFeSi_4O_{10}$) and other iron-bearing minerals were largely removed by passing the sample repeatedly through the Frantz Isodynamic Separator (20° tilt, 1° cant, 1.5 amp.). The fraction sinking in methylene iodide (G. = 3.3) and floating in Clerici solution (G. = 3.75) was nearly pure sanbornite. This fraction was passed through a narrow sorting chute under the binocular microscope and doubtful grains (some partly witherite) were removed by hand picking with the aid of a hollow-needle, suction-operated grain collector. The very fine material was removed in the heavy-liquid separations. Powder patterns prepared from random samples of the material thus purified showed no extraneous lines.

The density determined pycnometrically, using toluene, on 7 g. of the purified material is 3.71_2 g. cm.$^{-3}$. The mean density of four small (4 to

TABLE 3. ANALYSES OF SANBORNITE

	Weight per cent					
	I	II	III	IV	V	VI
SiO_2	44.13	44.19	44.16	43.92	42.2	Large amount
Al_2O_3	0.41	0.40	0.41		1.5	Small amount (X%)
Fe_2O_3	0.24	0.22	0.23		tr	Very small amount (0.X%)
CaO	0.20	0.20	0.20		0.1	Small amount (X%)
SrO	0.08	0.08	0.08		0.2	Very small amount (0.X%)
BaO	54.05	54.02	54.04	56.08	50.4	Large amount
MgO	0.27	0.29	0.28			Very small amount (0.X%)
H_2O-	0.15	0.15	0.15			[Traces (0.0X% to 0.000X%)
H_2O+	0.52	0.56	0.54			of Na, Cr, Mn and Ti]
Total	100.05	100.11	100.09	100.00	94.4	
Density (g. cm.$^{-3}$)			3.71_2	3.77	4.19	

I, II. Quantitative chemical analyses on 10 g. of purified sanbornite by Dr. R. Klemen, Vienna. Iron is reported as Fe_2O_3, no determination having been made of Fe^{+2} because of the small amount of iron present.

III. Mean of analyses I and II. Density determined pycnometrically using 7 g. of material.

IV. Calculated for $BaSi_2O_5$. Density calculated using sanbornite cell dimensions. Eskola (1922) reported a measured density for synthetic $BaSi_2O_5$ of 3.73 g. cm.$^{-3}$.

V. Rogers (1932): "analysis made upon one gram of carefully selected material which was, however, not quite pure." "The specific gravity determined on 0.3 g. is about 4.19. The value is approximate as the mineral contained a very small amount of included minerals."

VI. Spectrographic examination of purified sanbornite by Kennard and Drake, Los Angeles (Lab #19418). Rogers (1932) reported a spectrographic examination showing Ba, Sr, Ca, Si and Al.

20 mg.) fragments determined with the Berman balance is 3.70 ± 0.02. Quantitative chemical and qualitative spectrographic analyses are presented in Table 3.

The cell dimensions and pycnometric density given above and the composition in column III of Table 3 give the unit cell content (weight of unit atomic weight 1.6602×10^{-24} g.)

$$Ba_{3.80}Ca_{0.04}Sr_{0.01}Mg_{0.07}Fe^{+3}_{0.03}Al_{0.09}Si_{7.92}O_{19.93} \cdot 0.41H_2O.$$

The hydrogen, reported as water, is presumably non-essential. Calcium, strontium and barium ions commonly substitute for one another in other compounds at least to a slight extent, and hence may reasonably be grouped together. The presence of the much smaller and thus seemingly extraneous cations Mg^{+2}, Fe^{+3} (perhaps present as the larger Fe^{+2}) and Al^{+3} is not explained, although aluminum ions might replace a small proportion of silicon ions in the SiO_4 tetrahedra. This possibility will be considered more fully in the sequel on solid solution. Considering as essential only the barium, calcium, strontium, silicon and oxygen, and allowing for a small amount of quartz impurity, recalculating to twenty oxygen ions per unit cell gives

$$(Ba_{3.95}Ca_{0.04}Sr_{0.01})Si_{8.00}O_{20}$$
$$\text{Sum} = 4.00$$

(calculated density 3.75 g. cm.$^{-3}$), the total excess matter amounting to 2.93 per cent by weight. Thus sanbornite closely approaches in composition

$$Ba_4Si_8O_{20} = 4\ BaSi_2O_5$$

(formula weight 273.48, calculated density 3.77 g. cm.$^{-3}$).

Determination of the Structure

Preliminary

Intensities of diffraction maxima for the three principal zones were obtained from zero-layer Weissenberg photographs made with molybdenum radiation using multiple-film technique. Intensities were estimated by visual comparison of the diffraction spots with an arbitrary scale consisting of a film of the same type developed in the same manner, bearing a series of spots varying in intensity as a function of exposure time. Lorentz and polarization factors for equatorial photographs (Buerger, 1941) were applied, and absorption corrections were applied assuming the crystals, which were roughly equant, to be spheres (Evans and Ekstein, 1952). The Bond sphere grinder could not be used because of the extremely easy (001) cleavage. Absorption corrections were small owing to small crystal size (~0.2 mm. in greatest dimension), the moderately small absorption coefficient for molybdenum radiation, and the limited angular range (θ less than 45°) of spots obtainable using molybdenum radiation. No allowance was made for extinction.

At a late stage in the structure determination the scale factor, for conversion of observed structure amplitudes H (based on the arbitrary intensity scale) to absolute values $|F_o|$, was obtained for each zone, and an overall temperature coefficient B was evaluated. These were derived through least-squares analysis of $\log_e (H/|F_{c_0}|)$ as a linear function of $\sin^2 \theta$, where F_{c_0} is the calculated structure amplitude using scattering factors for ions at rest f_0. The value of $(H/|F_{c_0}|)$ at $\sin^2 \theta = 0$ was taken as the scale factor, and the slope of the line was taken to equal $-B/\lambda^2$. The value of B thus derived (0.48 Å^2) is an overall temperature coefficient, for which it is assumed that the mean displacement is the same for all ions and all directions in the crystal.

The temperature factors were applied to the calculated structure amplitudes F_{c_0} to give the values F_c listed with corresponding values of $|F_o|$ in Tables 4A-C.

The scattering factors f_0 used for Ba^{+2} are from values for Ba^0 adjusted by analogy with values for Ca^{+2} relative to those for Ca^0; values for Ba^0, Si^{+4} and O^{-2} are from *Internationale Tabellen* (1935). In view of the close approach of sanbornite to the ideal composition $BaSi_2O_5$, no allowances in scattering factors were made for substitution.

For lack of evidence to the contrary, it was assumed that the structure is centrosymmetric, hence the space group is *Pcmn*, and that it is not a defect structure, *i.e.*, all equivalent positions of any set are fully occupied. Thus it is required to distribute four barium, eight silicon and twenty oxygen ions among the positions (*International Tables*, 1952)

8 *d*	x, y, z; etc.
4 *c*	$x, 1/4, z$; etc.
4 *b*	1/2, 0, 0; etc.
4 *a*	0, 0, 0; etc.

TABLE 4A. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR 0*kl* REFLECTIONS

0*kl*	$\|F_o\|$	F_c	0*kl*	$\|F_o\|$	F_c	0*kl*	$\|F_o\|$	F_c
002	45*	+82	0, 2, 18	0	−37	062	77	−72
004	63	+63	032	89	+83	064	56	−54
006	0	−3	034	116	+110	066	0	−7
008	183	−165	036	154	+159	068	74	+76
0, 0, 10	87	−86	038	143	+134	0, 6, 10	93	+94
0, 0, 12	82	−82	0, 3, 10	0	−6	0, 6, 12	84	+90
0, 0, 14	91	−83	0, 3, 12	26	+26	0, 6, 14	53	+56
0, 0, 16	0	−10	0, 3, 14	95	−98	072	50	+62
0, 0, 18	0	+21	0, 3, 16	87	−102	074	51	+58
0, 0, 20	0	+42	0, 3, 18	0	−44	076	113	+119
0, 0, 22	89	+89	040	241	+223	078	94	+94
012	74*	−80	042	123	+121	0, 7, 10	0	+8
014	221	−203	044	46	+40	0, 7, 12	0	+12
016	188	−174	046	0	−10	0, 7, 14	79	−78
018	78	−78	048	108	−99	080	64	+61
0, 1, 10	62	−59	0, 4, 10	99	−99	082	109	+117
0, 1, 12	35	+38	0, 4, 12	76	−80	084	33	+29
0, 1, 14	64	+68	0, 4, 14	69	−64	086	0	−25
0, 1, 16	84	+83	0, 4, 16	0	−17	088	30	−29
0, 1, 18	77	+77	0, 4, 18	0	+18	0, 8, 10	105	−100
0, 1, 20	35	+36	052	41	−44	0, 8, 12	47	−74
020	70	−67	054	204	−185	092	35	−43
022	213	−205	056	108	−114	094	101	−106
024	75	−63	058	41	−39	096	88	−79
026	0	+8	0, 5, 10	74	−75	098	0	−50
028	29	+29	0, 5, 12	56	+63	0, 10, 0	151	−128
0, 2, 10	180	+163	0, 5, 14	43	+41	0, 10, 2	0	−41
0, 2, 12	100	+97	0, 5, 16	39	+62	0, 10, 4	0	−31
0, 2, 14	46	+47	0, 5, 18	83	+87	0, 10, 6	0	−10
0, 2, 16	24	+32	060	152	−154	0, 10, 8	68	+71

* Observed only on photographs made using copper radiation, for which the absorption coefficient in sanbornite is high.

Table 4B. Observed and Calculated Structure Amplitudes for *h0l* Reflections

h0l	$\|F_o\|$	F_c
002	48*	+ 82
004	65	+ 63
006	0	− 3
008	142	−165
0, 0, 10	80	− 85
0, 0, 12	89	− 82
0, 0, 14	98	− 82
0, 0, 16	0	− 10
0, 0, 18	0	+ 21
0, 0, 20	42	+ 38
0, 0, 22	82	+ 89
0, 0, 24	53	+ 38
101	0	− 6
102	0	− 24
103	97	−117
104	105	−152
105	72	+ 61
106	123	−154
107	0	+ 6
108	97	− 96
109	0	+ 9
1, 0, 10	109	−107
1, 0, 11	51	+ 43
1, 0, 12	70	+ 70
1, 0, 13	0	+ 12
1, 0, 14	69	+ 66
1, 0, 15	0	+ 5
1, 0, 16	86	+ 84
1, 0, 17	0	+ 10
1, 0, 18	93	+ 92
1, 0, 19	0	− 20
1, 0, 20	0	+ 14
1, 0, 21	0	− 9
1, 0, 22	0	+ 5
1, 0, 23	0	− 11
1, 0, 24	0	− 24
200	130	−193
201	59	+ 46
202	118	−134
203	63	+ 54
204	66	− 62
205	0	+ 10
206	58	+ 50
207	114	+124
208	89	+ 92
209	0	− 1
2, 0, 10	69	+ 73
2, 0, 11	0	− 2
2, 0, 12	79	+ 79
2, 0, 13	0	+ 13
2, 0, 14	56	+ 58
2, 0, 15	80	− 82
2, 0, 16	0	+ 14
2, 0, 17	0	− 9
2, 0, 18	0	− 19
2, 0, 19	0	− 30
2, 0, 20	49	− 38
2, 0, 21	0	− 17
2, 0, 22	68	− 64
2, 0, 23	0	+ 19
2, 0, 24	53	− 48
301	72	+ 76
302	74	+ 61
303	109	+105
304	48	+ 45
305	52	− 51
306	102	+100
307	0	− 2
308	100	+ 96
309	50	− 54
3, 0, 10	0	+ 10
3, 0, 11	78	− 85
3, 0, 12	0	+ 2
3, 0, 13	29	− 26
3, 0, 14	72	− 65
3, 0, 15	22	− 21
3, 0, 16	81	− 72
3, 0, 17	16	− 19
3, 0, 18	34	− 38
3, 0, 19	30	+ 41
3, 0, 20	31	− 32
3, 0, 21	26	+ 35
3, 0, 22	19	+ 8
3, 0, 23	0	+ 22
3, 0, 24	27	+ 18
400	43	+ 28
401	21	− 22
402	118	+107
403	68	− 59
404	0	+ 10
405	75	− 72
406	62	− 44
407	85	− 92
408	0	− 4
409	44	− 39
4, 0, 10	81	− 73
4, 0, 11	0	− 6
4, 0, 12	50	− 42
4, 0, 13	0	+ 26
4, 0, 14	0	− 8
4, 0, 15	66	+ 73
4, 0, 16	38	− 29
4, 0, 17	39	+ 47
4, 0, 18	0	+ 4
4, 0, 19	31	+ 38
4, 0, 20	32	+ 44
4, 0, 21	0	+ 14
4, 0, 22	0	+ 15
4, 0, 23	0	− 12
4, 0, 24	33	+ 39
501	87	− 95
502	34	− 28
503	46	− 47
504	0	− 3
505	14	− 19
506	62	− 46
507	36	+ 47
508	60	− 49
509	67	+ 66
5, 0, 10	0	+ 11
5, 0, 11	58	+ 55
5, 0, 12	29	− 25
5, 0, 13	67	+ 62
5, 0, 14	54	+ 41
5, 0, 15	25	+ 28
5, 0, 16	44	+ 38
5, 0, 17	0	− 9
600	0	+ 3
601	0	+ 5
602	44	− 33
603	57	+ 54
604	0	− 2
605	75	+ 87
606	0	+ 18
607	49	+ 50
608	0	+ 2
609	63	+ 66
6, 0, 10	0	+ 11
6, 0, 11	0	+ 4
6, 0, 12	0	+ 5
6, 0, 13	44	− 53
6, 0, 14	0	+ 5
6, 0, 15	0	− 34
6, 0, 16	0	+ 3
6, 0, 17	56	− 70
701	67	+ 85
702	0	− 9
703	0	+ 16
704	0	− 5
705	35	+ 28
706	0	− 9
707	36	− 41
708	0	+ 4
709	41	− 54
7, 0, 10	0	+ 5
7, 0, 11	26	− 44
7, 0, 12	0	− 6
7, 0, 13	38	− 45
800	0	+ 8
805	46	− 61

* Observed only on photographs made using copper radiation, for which the absorption coefficient in sanbornite is high.

TABLE 4C. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR $hk0$ REFLECTIONS

$hk0$	$\|F_o\|$	F_c	$hk0$	$\|F_o\|$	F_c	$hk0$	$\|F_o\|$	F_c
020	68	− 66	2, 12, 0	40	− 44	590	0	− 18
040	214	+221	2, 14, 0	41	+ 47	5, 11, 0	0	+ 17
060	167	−152	310	75	+ 83	600	0	+ 3
080	73	+ 60	330	135	−133	620	0	+ 19
0, 10, 0	127	−128	350	44	+ 38	640	0	− 11
0, 12, 0	48	+ 46	370	89	−100	660	0	− 1
0, 14, 0	49	− 63	390	52	+ 46	680	0	− 21
110	208	−219	3, 11, 0	39	− 50	6, 10, 0	0	− 3
130	130	+115	3, 13, 0	0	+ 44	6, 12, 0	0	− 7
150	216	−176	400	38	+ 28	710	0	− 8
170	82	+ 86	420	100	−107	730	0	+ 8
190	89	− 80	440	51	+ 63	750	0	− 7
1, 11, 0	79	+ 91	460	45	− 37	770	0	+ 5
1, 13, 0	41	− 35	480	66	+ 81	790	0	− 8
200	180	−193	4, 10, 0	0	− 19	800	0	+ 8
220	81	+ 81	4, 12, 0	0	+ 45	820	0	+ 31
240	153	−130	510	0	− 23	840	0	− 6
260	100	+ 88	530	78	+ 83	860	0	+ 7
280	70	− 70	550	0	+ 10	880	0	− 22
2, 10, 0	84	+ 73	570	58	+ 64	8, 10, 0	0	− 2

In silicate structures each silicon ion is surrounded by four oxygen ions arranged at the vertices of a nearly regular tetrahedron. In sheet silicates each such SiO_4 tetrahedron shares one oxygen ion with each of three other tetrahedra, leaving one unshared oxygen ion per tetrahedron, and forming continuous sheets having an overall Si/O ratio of $\frac{2}{5}$.* The fact that the Si/O ratio in sanbornite is $\frac{2}{5}$ and that the mineral has a very prominent cleavage normal to the largest cell dimension suggests that it has a silicate sheet structure with the sheets lying parallel to (001).†

From symmetrical and spatial considerations it was possible to devise a satisfactory arrangement of four SiO_4 tetrahedra in each of two undulating $(Si_4O_{10})^{-4}$ sheets per unit cell lying parallel to (001) at $z=\frac{1}{4}$ and $\frac{3}{4}$. The tetrahedra in this arrangment possessed a certain range of freedom in their orientation, and in the final structure they were found to lie within this predicted range. This postulated configuration of the sheets left sufficient space for the barium ions only between the sheets, where they might be expected to lie anyway.

Patterson projections

Two-dimensional Patterson projections on (100) and (001), shown in

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* Pabst (1943) has pointed out that there are other geometrical possibilities of linking tetrahedra so as to give an Si/O ratio of 2/5 but not forming sheets.

† Rogers (1932) recognized the likelihood of sanbornite having a sheet structure and without benefit of x-ray data described a pseudohexagonal sheet structure which he pictured as "probable".

Figs. 1 and 2, respectively, were made by the photographic method of Huggins (1944). The most intense maxima are attributed to barium-barium vectors in view of the high scattering power of barium relative to silicon and oxygen ions. In the (100) projection (Fig. 1) the two most intense maxima lie at approximately $\frac{1}{2}$ *b*, 0.08*c* and $\frac{1}{2}$ *b*, 0.41*c*. Because vector components parallel to *c* have values other than 0 and $\frac{1}{2}$, the four barium ions cannot occupy positions of sets *a* or *b*, leaving only positions of set *c*. Equivalent positions of set *c* are related by vectors whose components parallel to *a*, *b* and *c* may be expressed in terms of coordinates *x*, *y* and *z* as follows:

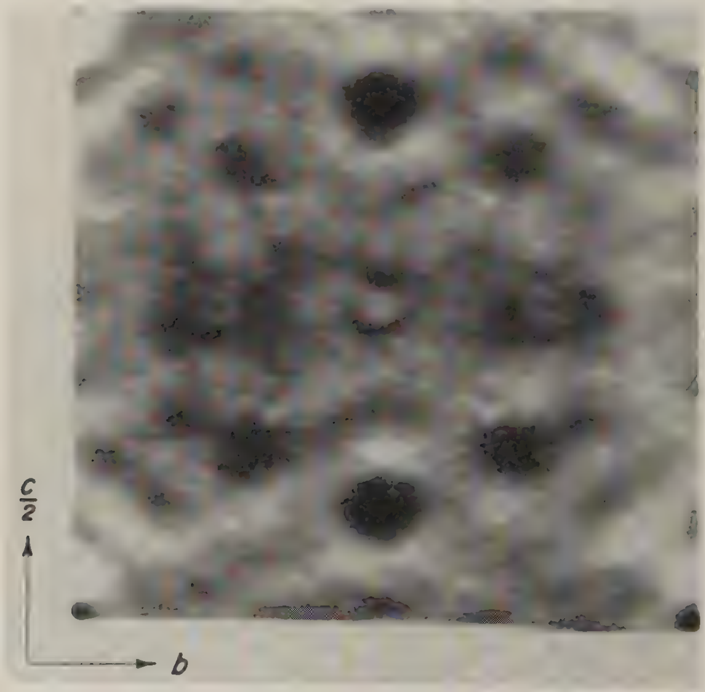

FIG. 1. Patterson projection of the sanbornite structure on (100).

$$2x, 1/2, 2z; 1/2, 1/2, 1/2 - 2z; 1/2 - 2x, 0, 1/2$$

The vector components parallel to *c* give two non-equivalent sets of four equivalent values for z_{Ba}: $(0; \frac{1}{2}) \pm \sim 0.04_2$ and $(0; \frac{1}{2}) \pm \sim 0.20_5$. In the (001) projection (Fig. 2) the one intense spot at approximately $\frac{1}{2}$ *a*, $\frac{1}{2}$ *b* appears elongated parallel to *a*, suggesting overlap of maxima whose vector components parallel to *a* are close to $\frac{1}{2}$. The interequivalent-position vector components given above show that a maximum must appear in this projection at $\frac{1}{2}$ a, $\frac{1}{2}$ b, but the absence of intense maxima elsewhere in the projection is explained only if $x_{Ba} = (0; \frac{1}{2}) \pm \sim\frac{1}{4}$.

Fourier projections and use of a model

Assuming the signs of $F(0kl)$ for the stronger reflections in the range k and $l = 0$ to 8 to be determined solely by the barium ions (an assumption subsequently vindicated) and taking $y_{Ba} = \frac{1}{4}$, $z_{Ba} = 0.04_2$, a Fourier projection on (100) was prepared using the strip method of Lipson and Beevers (1936) with a hand calculating machine. The symmetry of the (100) projection necessitates summing only over the range 0 to $\frac{1}{4}$ b and 0 to $\frac{1}{2}$ c, and any one of the four equivalent values $z_{Ba} = (0; \frac{1}{2}) \pm 0.04_2$ may be tentatively assumed. The resulting electron density map (Fig. 3) shows two large spurious peaks along $y = \frac{1}{4}$ and displacement and poor resolution of some of the expected peaks owing largely to strong termination effects. It can be shown that if z_{Ba} were taken to be one of the four equivalent values $(0; \frac{1}{2}) \pm 0.20_8$ instead of $(0; \frac{1}{2}) \pm 0.04_2$ an identical map would result but with the origin displaced $\frac{1}{4}$ c; the symmetry elements of space group *Pcmn* projected on (100) are compatible with

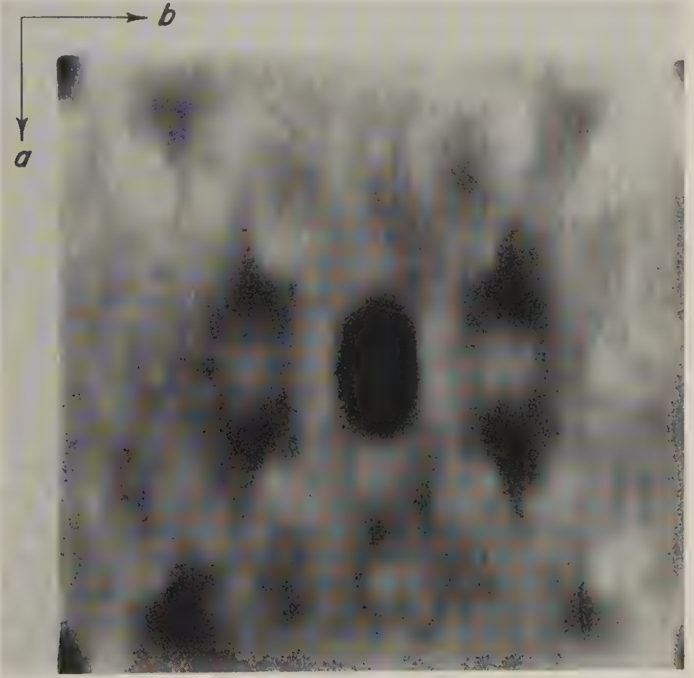

FIG. 2. Patterson projection of the sanbornite structure on (001).

either setting. This projection establishes, however, either that $z_{Ba}=(0;\ \frac{1}{2})\pm\sim0.04_2$ and $z_{sheets}=\frac{1}{4}$ and $\frac{3}{4}$ or that $z_{Ba}=(0;\ \frac{1}{2})\pm\sim0.20_8$ and $z_{sheets}=0$ and $\frac{1}{2}$.

A three-dimensional working model was constructed of cardboard, assuming the SiO_4 tetrahedra to be regular tetrahedra 2.70 Å on an edge and based on the ionic distribution

Ba, O_I	in	4 *c*	x, 1/4, z; etc.
Si, O_{II}, O_{III}	in	8 *d*	x, y, z; etc.

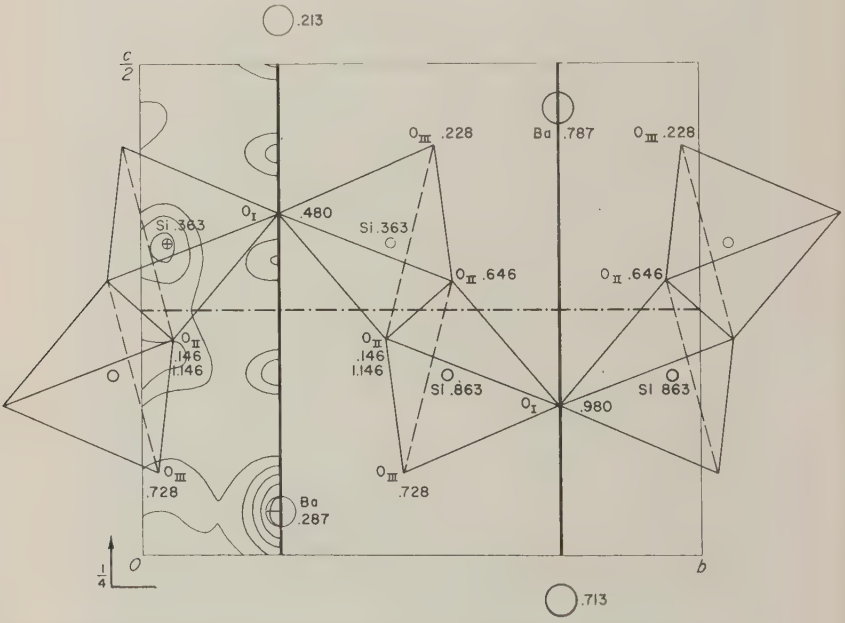

FIG. 3. Projection of the sanbornite structure on (100). Contour interval (on an arbitrary scale) around barium ion is four times that of rest of projection.

This model aided greatly in correlating shifts in oxygen and silicon coordinates along all three axes. Using information from the (100) Patterson and Fourier projections together with trial-and-error adjustment controlled by this model, a set of approximate y and z parameters was chosen, yielding a residual factor $R(0kl)=0.30$, where $R=\Sigma\,||F_o|-|F_c||/\Sigma|F_o|$ omitting $||F_o|-|F_c||$ if $F_o=0$. Thus it was established that $z_{sheets}=\frac{1}{4}$ and $\frac{3}{4}$, and for $y_{Ba}=\frac{1}{4}$, $z_{Ba}=(0;\ \frac{1}{2})+\sim0.04_2$.

Symmetry permits the two parallel silicate sheets per unit cell to "slide" over one another in a direction parallel to a, subject only to the condition that a shift of one sheet be accompanied by an equal but opposite shift of the other. Having available approximate y and z parameters, further use of the model gave approximate tetrahedral x' parameters relative to one sheet, giving the configuration of the sheet but not its position along a. Trial-and-error shifting of x_{Ba} and of the sheets along a led to a set of parameters yielding $R(h0l)=0.28$.

A Fourier projection on (010) was then prepared using signs of $F(h0l)$ given by the x and z parameters determined so far. It is only necessary to sum over the range 0 to $\frac{1}{2}$ along both axes. From the parameters given by this projection were obtained the signs of terms previously of uncertain or incorrect sign, and these terms were included in a new projection (Fig. 4). From this refined projection were taken, after further trial-and-error adjustment, the final x and z parameters.

From the x, y and z parameters thus derived (Table 5) have been calculated the structure amplitudes F_c (to which have been applied temperature factors) listed in Tables 4A–C with corresponding values of $|F_o|$. These calculated and observed structure amplitudes yield the residual factors (omitting terms for which $F_o=0$) $R(0kl)=0.069$, $(Rh0l)=0.135$, $R(hk0)=0.098$, and an overall value (221 terms) of 0.101. These acceptably small residual factors and the generally satisfactory agreement between calculated and observed structure amplitudes suggest that the coordinates are known with sufficient accuracy to firmly establish the structure.

Discussion of the Structure

The structure of sanbornite given by the coordinates listed in Table 5 is shown projected on (100), (010) and (001) in Figs. 3, 4 and 5, respectively. In these figures the larger circles represent barium, the smaller circles silicon and the vertices of the outlined tetrahedra oxygen ions. The unit cell or indicated fraction thereof is outlined, and minimum symmetry elements are shown.

The oxygen ions of type I lie in the m planes, which are parallel to (010) at $y=\frac{1}{4}$ and $\frac{3}{4}$. Each of these oxygen ions is shared by two SiO_4 tetrahedra which are thus mirror images of one another. Each tetrahedron of such a mirror-image pair shares its two oxygen ions of type II with two other tetrahedra, each of which in turn belongs to another mirror-image pair (best seen in Fig. 5). The one oxygen ion of type III per tetrahedron is unshared, and as to be expected, the shortest silicon-oxygen distance in the tetrahedra (Table 6) is that between the silicon and this unshared oxygen ion. Adjacent mirror-image pairs are related by diagonal glide reflection across one of the two n planes parallel to (001) at $z=\frac{1}{4}$ and $\frac{3}{4}$. This results in continuously linked, distorted, six-membered rings of tetrahedra, forming undulating sheets of indefinite extent which lie parallel to (001) at $z=\frac{1}{4}$ *or* $\frac{3}{4}$ and have an overall Si/O

TABLE 5. FINAL COORDINATES OF IONS IN SANBORNITE

(Expressed as fractions of cell edges)

	x	y	z
Ba in 4 c	0.287	1/4	0.045
Si in 8 d	0.363	0.050	0.317
O_I in 4 c	0.480	1/4	0.348
O_{II} in 8 d	0.146	0.060	0.220
O_{III} in 8 d	0.228	0.970	0.416

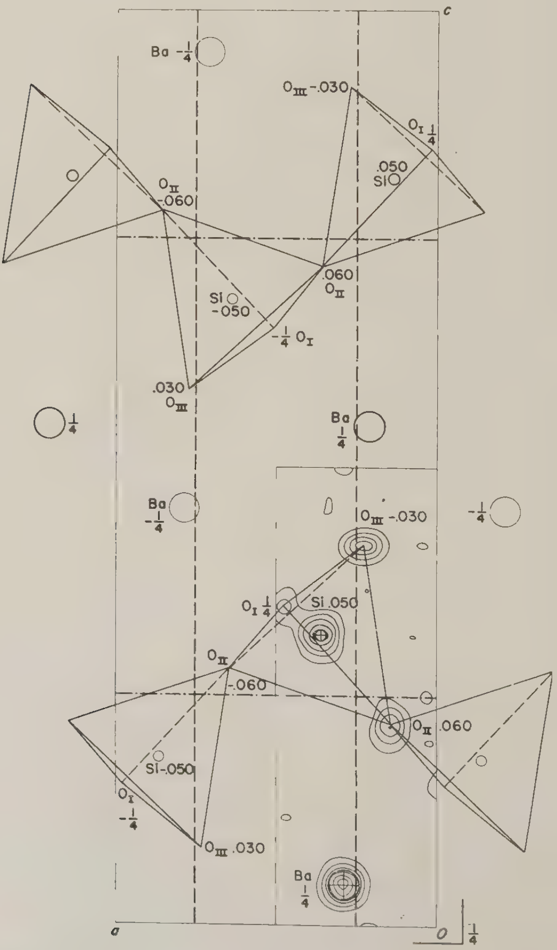

FIG. 4. Projection of the sanbornite structure on (010). Contour interval (on an arbitrary scale) around barium ion is four times, around silicon ion two times, that of rest of projection.

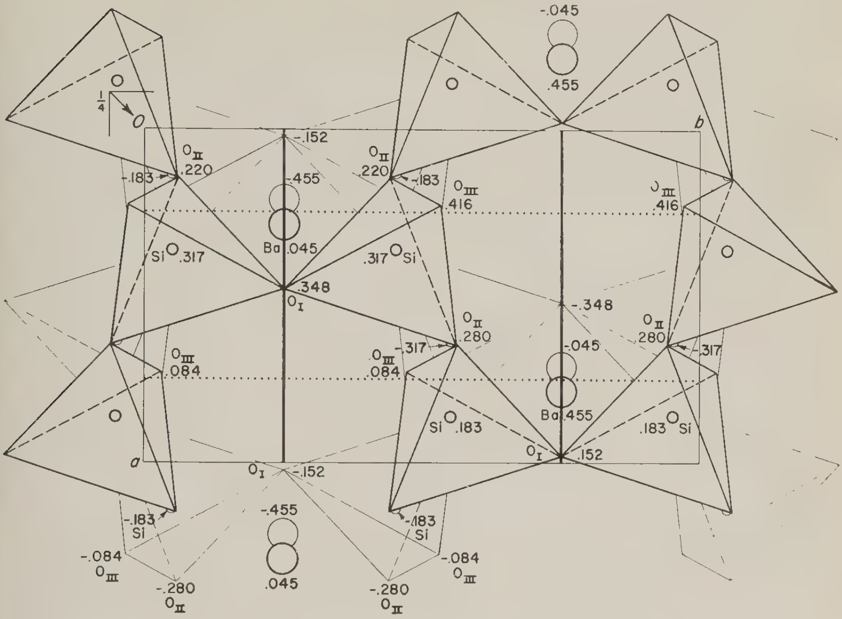

FIG. 5. Projection of the sanbornite structure on (001).

TABLE 6. INTERIONIC DISTANCES IN SANBORNITE

Edges of SiO_4 tetrahedra	
O_I–O_{II}	2.67 Å
O_I–O_{II}	2.74
O_I–O_{III}	2.62
O_{II}–O_{II}	2.62
O_{II}–O_{III}	2.68
O_{II}–O_{III}	2.77
Shortest intralayer intertetrahedral O–O distance:	
O_{II}–O_{II}	2.92
Shortest interlayer O–O distance:	
O_{III}–O_{III}	3.14
Si–O_I	1.68
Si–O_{II}	1.64
Si–O_{II}	1.65
Si–O_{III}	1.60
Ba–O_I	2.94
Ba–O_{II}	2 at 2.86
Ba–O_{III}	2 at 2.74
Ba–O_{III}	2 at 2.77
Ba–O_{III}	2 at 3.14
Next shortest Ba–O distance	
Ba–O_I	4.20

ratio of $\frac{2}{5}$. Glide reflection across the c planes, which are parallel to (100) at $x=\frac{1}{4}$ and $\frac{3}{4}$, produces two $(Si_4O_{10})^{-4}$ sheets per unit cell lying parallel to (001) at $z=\frac{1}{4}$ and $\frac{3}{4}$. Unshared vertices of tetrahedra (oxygen ions of type III) point out in pairs alternately from one side and then the other of each sheet.

The four barium ions per unit cell lie in equal numbers roughly half way between each successive pair of sheets. Each barium ion is surrounded by seven near oxygen ions (Table 6) of which the four nearest, as to be expected, are unshared oxygen ions of type III, two belonging to the superjacent sheet and two to the subjacent sheet.* The barium ions satisfy the excess negative charge of the sheets and thus hold them together.

TABLE 7. COMPARISON OF SOME INTERIONIC DISTANCES

Structure	Edges of SiO_4 tetrahedra	Si–O	Ba–O
Sanbornite, $BaSi_2O_5$ (This paper)	6, 2.62–2.77 Å	4, 1.60–1.68 Å	7, 2.74–2.94 Å 2, 3.14 Å
Gillespite, $BaFeSi_4O_{10}$ (Pabst, 1943)	6, 2.58–2.67 Å	4, 1.56–1.64 Å	2.73, 2.98 Å
β-$Na_2Si_2O_5$ (Grund, 1954)	12, 2.50–2.75 Å	8, 1.50–1.65 Å	
Paracelsian, $BaAl_2Si_2O_8$ (Smith, 1953)			7, 2.69–2.85 Å 2, 3.33 Å
Tetragonal $BaTiO_3$ (Evans, 1951)			2.782, 2.826, 2.896 Å
Sum of ionic radii (*Internationale Tabellen*, 1935)		1.59 Å (four coordination)	2.75 Å (six coordination)

The interionic distances in sanbornite (Table 6) are in satisfactory agreement with corresponding distances found in other structures as compared in Table 7.

RELATED STRUCTURES

The mineral gillespite ($BaFeSi_4O_{10}$) is closely related to sanbornite ($Ba_2Si_4O_{10}$) in composition and occurrence, and also possesses a silicate sheet structure (Pabst, 1943), but the two structures have important differences. Gillespite is tetragonal with two *double* sheets per unit cell made up of linked, *four*-membered rings of SiO_4 tetrahedra. The barium ions in gillespite, as in sanbornite, lie between the sheets and are associated with oxygen ions of both adjacent sheets, but each ferrous ion in gillespite is associated with oxygen ions of only one sheet.

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* Smith (1953) also found seven near oxygen ions about each barium ion in paracelsian, $BaAl_2Si_2O_8$.

Schaller (1929) and Pabst (1943, 1955) found that the iron and barium can be completely leached out of gillespite with hydrochloric acid without complete physical disintegration. The initially bright-red flakes become colorless and the density and mean refractive index drop markedly, but the optical character and outward shape are retained, and Laue and precession photographs show that the essential silicate sheet structure persists. Sanbornite treated with even dilute hydrochloric acid quickly swells up into low-birefringent, x-ray-amorphous shreds. The greater stability of the gillespite sheet structure on leaching may arise from its having two cations, beside silicon, which are differently linked to the silicate sheets; these might be selectively removed in successive stages of leaching. Possibly the double sheets of four-membered rings of tetrahedra in gillespite are mechanically more rigid than the single sheets of six-membered rings of tetrahedra in sanbornite

The only silicates having the composition $R_2Si_2O_5$ known to the writer are those in which $R=Ba_{1/2}$, Li, Na, K, Rb or Cs (Ramberg, 1954). It is particularly interesting that $CaSi_2O_5$ and $SrSi_2O_5$, which might be expected to be isomorphous with sanbornite, are not known. Comparison of simple disilicates for which sufficient x-ray data are available (Table 8) reveals some striking similarities. However, the crystal structures of only two of these, sanbornite and β-$Na_2Si_2O_5$, have been determined. The β-$Na_2Si_2O_5$ structure (Grund, 1954), although monoclinic, resembles the sanbornite structure in that it consists of two undulating, single $(Si_4O_{10})^{-4}$ sheets per unit cell lying parallel to the very prominent cleavage [in this case (100)], with the larger cations lying in equal numbers between each successive pair of sheets and associated with oxygen ions of both sheets. The arrangement of SiO_4 tetrahedra in the sheets is quite different, although unshared tetrahedral vertices point out alternately from both sides of each sheet as in sanbornite. Four of the eight sodium ions per unit cell are surrounded by six near oxygen ions, the remainder by five.

In summary, sanbornite, gillespite, β-$Na_2Si_2O_5$ and possibly all of the other alkali disilicates have in common the following features distinguishing them as a group from all other known phyllosilicates: (1) they contain no hydrogen (unique to this group); (2) successive sheets are held together by the larger cations (unique except for micas, brittle micas and apophyllite); and (3) tetrahedral vertices point out from both sides of the sheets (unique except for apophyllite). Gillespite may be regarded as comprising a subgroup because (1) the sheets are double and (2) it contains more than one cation beside silicon, one of which is associated with only one sheet.

SOLID SOLUTION

As mentioned in the preceding section, no calcium or strontium analog of sanbornite is known. The analyses of sanbornite (Table 3) show very small amounts of calcium and strontium which are presumably replacing barium, but the limits of such substitution have not been assessed. Determination of these limits seems worthy of further study, especially with regard to strontium.

TABLE 8. COMPARISON OF SOME PHASES OF COMPOSITION $R_2Si_2O_5$

(Crystallographic elements oriented for comparison with β-$Na_2Si_2O_5$)

Cell content	Space group	a_0	b_0	c_0	β	Prominent cleavage	Volume per O^{-2}
$Ba_4Si_8O_{20}$ (sanbornite)	*Pnam*	13.53 Å	4.63 Å	7.69 Å	—	{100}	24.1 Å^3
α-$Na_8Si_8O_{20}$	(*1*) *Pnam*	15.45	4.909	6.428	—	{100}	24.4
β-$Na_8Si_8O_{20}$	(*1*) P2_1/*a*	12.307	4.849	8.124	104.12°	{100}	23.5
	(*2*) *P*2_1/*a*	12.26	4.80	8.07	104°18′	{100}	23.0
$Li_8Si_8O_{20}$	(*1*) *Bbmb* or *Bb2b*	14.66	4.806	5.80	—	{100}	20.4

(*1*) Donnay and Donnay (1953).
(*2*) Grund (1954).

The system $BaSi_2O_5-Na_2Si_2O_5$ was investigated by Greene and Morgan (1941) who found only a simple eutectic (32 weight per cent $BaSi_2O_5$, 797° C.) and no intermediate compounds or mix crystals. Spectrographic analyses of sanbornite show virtually complete absence of the alkali elements, but the surrounding rocks are low in these elements also. In a limited substitution of two alkali ions for one barium ion in the sanbornite structure, one alkali ion could possibly occupy each former barium position, but there are apparently no holes elsewhere in this structure which can suitably accommodate the other alkali ion.

In a study of the system $BaO-SiO_2$ Eskola (1922) reported a "complete series of solid solutions" between the "very perfectly isomorphous" end members $BaO\cdot 2SiO_2$ ($BaSi_2O_5$) and $2BaO\cdot 3SiO_2$ or $BaO\cdot 1.5SiO_2$. Thomas (1950) did not consider $BaO\cdot 1.5SiO_2$ to be a compound, and extended the range of solid solution to $BaO\cdot \sim 1.4SiO_2$. Levin and Ugrinic

(1953) concluded that $BaO \cdot 1.5SiO_2$ was a compound and stated that "$BaO \cdot 2SiO_2$ and $2BaO \cdot 3SiO_2$ show unusual behavior for refractory oxide systems in that they form a complete isomorphous solid solution series without a maximum or a minimum", but they also stated that optical properties and powder patterns of the primary phase crystals did not differ significantly from those of pure $BaO \cdot 2SiO_2$ (however, see observations regarding their powder pattern in the introductory section of the present paper). Complete solid solution between $BaO \cdot 2SiO_2$ and $2BaO \cdot 3SiO_2$ was also reported by Toropov, Galakhov and Bondar (1955). It seems certain from the physical properties given that Bowen (1918), Eskola (1922), Greene and Morgan (1941), Austin (1947), Thomas (1950), and Toropov, Galakhov and Bondar (1955) all obtained $BaSi_2O_5$ of sanbornite structure on heating a mixture of this composition, as did the writer. However, it is difficult to envisage in the sanbornite structure a reasonable mechanism of removal, substitution or addition of silica or baryta which could account for such serious apparent deficiencies in silica (up to one fourth) or excesses in baryta (up to one third) as have been reported.

Thomas (1950) reported a limited solid solution between $BaO \cdot 2SiO_2$ ($BaSi_2O_5$) and $BaO \cdot Al_2O_3 \cdot 2SiO_2$ ($BaAl_2Si_2O_8$, celsian) to the extent of $BaO \cdot \sim 0.22Al_2O_3 \cdot 2SiO_2$, and another solid solution between $BaO \cdot 1.5SiO_2$ and $BaO \cdot Al_2O_3 \cdot 2SiO_2$. Similar conclusions were drawn by Toropov, Galakhov and Bondar (1955) in a reinvestigation of this same portion of the system baryta-alumina-silica. In accounting for these findings regarding $BaSi_2O_5$, Al^{+3} ions might be expected to replace some of the Si^{+4} ions in the SiO_4 tetrahedra, as is commonly the case in aluminosilicates. The resulting deficiency in positive charge might be compensated in one or both of two ways: (1) Substitutions of Al^{+3} for Ba^{+2} equal in number to the substitutions of Al^{+3} for Si^{+4} in the tetrahedra. Such replacement would probably be very limited considering the great disparity in size between the barium ion and all the common trivalent cations. (2) Accomodation of one aluminum ion in some hole in the structure for each three substitutions of aluminum for silicon ions in the tetrahedra.

Clearly these solid solutions involving the sanbornite structure need reinvestigation with attention to structural implications.

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WELDED TUFF FROM DEEP-WELL CORES FROM CLINCH COUNTY, GEORGIA*

CLARENCE S. ROSS,
U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

A suite of drill cores from a depth of about 4,000 feet from Clinch County, southeastern Georgia, merits description because the cores disclose a type of volcanism not previously recognized in the region, and also because they contribute to the much broader story of igneous activity in the Georgia-Florida region.

The record of volcanism begins with a fine-grained volcanic conglomerate composed of andesite and welded tuff fragments of dacitic character. These are partly rounded and have been transported to their present position. Above the conglomerate is about 35 feet of rhyolitic welded tuff which represents deposition directly from an ash flow, which has been replaced by laumontite. Above the ash flow tuffs is a recurrence of the transported volcanic conglomerate materials.

Low-grade metamorphism has affected the volcanic materials, but without detracting from the relationships.

INTRODUCTION

A deep well drilled in southeastern Georgia in 1952 presented an excellent set of drill cores extending through volcanic materials. The cores became available for study by the U. S. Geological Survey and were referred to me by the late Josiah Bridge. The well is known as the Lem Griffith's well No. 1 and is in Clinch County, Georgia, about 12 miles east of Fargo.

The cores of the Clinch County well merit description because they disclose a type of volcanic activity not previously recognized in the region, and also because they contribute to the much broader story of igneous activity in southeastern Georgia and much of Florida. The wide extent of deeply buried volcanic materials in the Georgia-Florida region has been revealed in the course of investigations of possible oil resources, and we have to thank the oil geologists connected with these studies for much valuable information.

The core samples of the Clinch County well extended from a depth of 3,981 to 4,119 feet, and present about 138 feet of volcanic materials. Drill cuttings were available for study from depth ranging between 3,830 and 3,870 feet, and between 4,330 and 4,470 feet. Electric log characteristics and a study of cutting samples by Esther R. Applin, U. S. Geological Survey (personal communication) indicated that rhyolitic rocks were penetrated at a depth of about 3,843 feet.

Three types of volcanic materials are recorded in these cores. These and the overlying and underlying clastic and detrital materials may be briefly described as follows, beginning with the lowermost available materials.

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* Publication authorized by the Director, U. S. Geological Survey.

Most of the chips from drill cuttings between 4,470 and 4 330 feet are shalelike material, composed of different proportions of igneous detrital debris, but a few represent volcanic rock fragments. The significance of the volcanic fragments is not clear, as they may represent material derived from higher levels. However, one core sample taken at a depth of 4,348 feet was a fine-grained dense black shale with no recognizable ash shards. Microscopic examination of this and the chip samples of shale indicated only slight metamorphism and no significant characteristics.

The lowermost core sample in the interval 3,981 to 4,119 feet is composed of andesitic and dacitic volcanic rock fragments. Many of these, in particular the dacitic ones, are partly rounded. The aggregate of volcanic debris is best described as fine-grained volcanic conglomerate. The petrology of these rocks will be discussed in the following section.

The material lying between 4,101 and 4.059 feet represents rhyolitic welded tuff. However, the lower 9 feet of this section is composed of a mixture of the andesitic and dacitic materials and rhyolitic welded tuff. The materials lying above the welded rhyolitic tuff (4,057 to 3,986 feet) show several lenses of fine volcanic conglomerate similar to that in the lower part of the section. Other parts are best described as a shalelike volcanic graywacke. The volcanic conglomerate reoccurs at intervals up to at least 3,830 feet, with finer detrital material intervening. Some thin sections show a dominance of plagioclase grains which seem to have been derived from the andesite rock source.

Petrology of the Clinch County Cores

The fine-grained volcanic conglomerate is composed of andesite and dacite rock fragments that have been transported and so intimately intermixed that their relative age is indeterminable.

Andesite

The andesite rock fragments range in size from a fraction of a millimeter up to about 4 mm. in diameter. Some have a very fine-grained trachytic texture and others contain plagioclase crystals as much as 1 mm. in diameter. Free plagioclase grains of equal size are abundant, especially near the upper part of the drill core. The free crystals are in part euhedral in outline but many of them are angular. The feldspar has undergone alteration as described in a later section of this paper. Ferromagnesian groundmass material has altered to dark pigment, and a few altered ferromagnesian phenocrysts are now a serpentinelike material. Some of the andesite fragments contain spherical gas cavities now filled with celadonite or chlorite. Abundant minute areas of leucoxene indicate that the andesite originally contained finely disseminated ilmenite. The andesite rock fragments show none of the welded tuff structures that characterize the dacite.

Dacite

Rock fragments of dacitic character form a large but varying proportion of the detrital materials both below and above the welded rhyolite tuff. These rock fragments are as much as 5 mm. in diameter, and commonly show distinct rounding. The color is usually a cinnamon buff (Ridgeway). A wide variety of the structures commonly characterizing high-silica volcanic rocks is observable and includes fragments of large spherulites, fine grained aggregates of spherulites, and fragments characterized by swarms of fine grained lathlike plagioclase crystals that give a trachytic structure. The most significant fragments are those that show welded tuff structure as illustrated in Fig. 1. The shards there represented are without distortion, but in most of the grains there is marked compression and distortion of the ash structure. A few grains show dis-

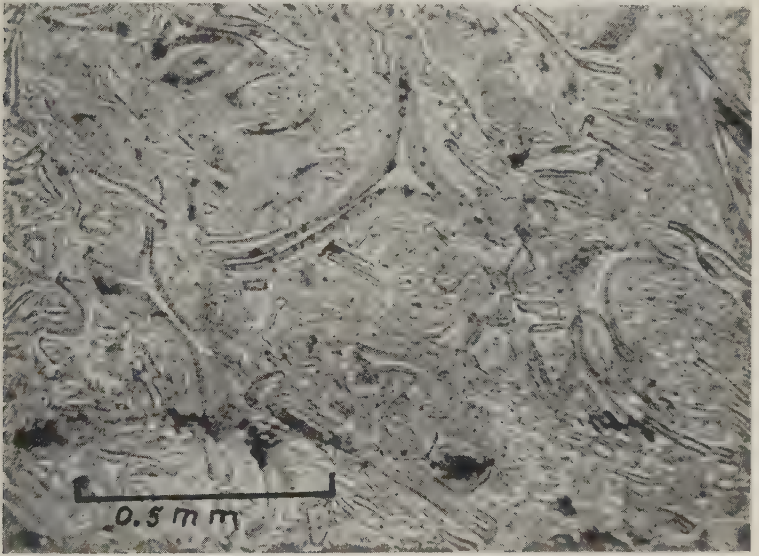

FIG. 1. Welded tuff from a deep well, Clinch County, Georgia. Dacitic welded tuff. The zoned structure resulting from devitrification and the development of cristobalite and feldspar is well represented in the central shard.

tortion of pumice grains. The shards retain the axiolitic structure resulting from a fine grained parallel intergrowth of feldspar and cristobalite. Whether any cristobalite remains is problematical. In some of the shards a welded tuff structure may have been destroyed during devitrification, which occurs as a result from the development of spherulitic structures and the coarser grained devitrification products. Many of the shards show a distinct flow structure and it seems probable that both welded tuff and flow rocks are represented by the dacite rock fragments.

Most of the welded tuff fragments show the structures commonly resulting from the disruption of roughly equidimensional glass bubbles, and include lune-shaped fragments, cusps bounded by segments of three contiguous bubbles, curved plates, and pumice fragments. In many rock fragments there has been marked compression and alignment of the shards, but these retain distorted traces of the aforementioned ash structures. The dacite differs from the andesite in the absence of phenocrysts in most of the rock fragments. Sparse plagioclase phenocrysts are now sodic, but the extent of change due to alteration is unknown. The crystal habit suggests that they were more sodic than the abundant plagioclase phenocrysts of the andesite. Quartz phenocrysts are rarely present. No ferromagnesian silicates are observable, either as phenocrysts or in the groundmass.

Welded rhyolite tuff

The core samples lying between 4,101 and 4,057 feet comprise the second type of welded tuff. This horizon differs in essential ways from the horizon below and above, and is characterized by material of distinct petrographic character. The basal part of this horizon, lying between 4,101 and 4,092 feet, contains a large proportion of the dacitic and andesitic fragments previously described. Evidently the ash flow emplacing the rhyolite welded tuff overrode the unconsolidated materials below and incorporated a large proportion of them into the basal part of the rhyolite ash flow. The rhyolite type of shard fills interstices between the andesite-dacite rock fragments. The shards of this interstitial ash material were derived from fractured glassy bubble walls and show only moderate distortion, but collapsed pumice fragments were much more plastic and lenses of pumice bend around and are constricted between rock fragments.

The upper 35 feet of the welded tuff section (4,092 to 4,057 feet) represents almost pure rhyolitic shard material. Most of these shards have the forms resulting from the disruption of a vesiculated glass, as illustrated in Fig. 2. These comprise arcs of bubble walls, slightly curved plates, cusps bounded by arcs of circles, and Y shaped fragments representing the juncture of three bubbles. Unbroken bubbles are not rare.

Platelike shards derived from ruptured pumice fragments are also present, and a few pumice fragments show distortion as in the lowest part of the welded rhyolite. Between these shards is a matrix material representing volcanic dust. The shards have dimensions of the order of 0.4 mm and represent a rather coarse-grained ash.

Phenocrysts of feldspar and quartz form only a few per cent of the rock. The feldspar is clouded by minute flakes of sericitic mica. The plagioclase has no doubt become more sodic by alteration as discussed in the section on alteration. Some of the feldspar was probably sanidine. No ferromagnesian phenocrysts are present, and the rock represents a typical welded rhyolite tuff.

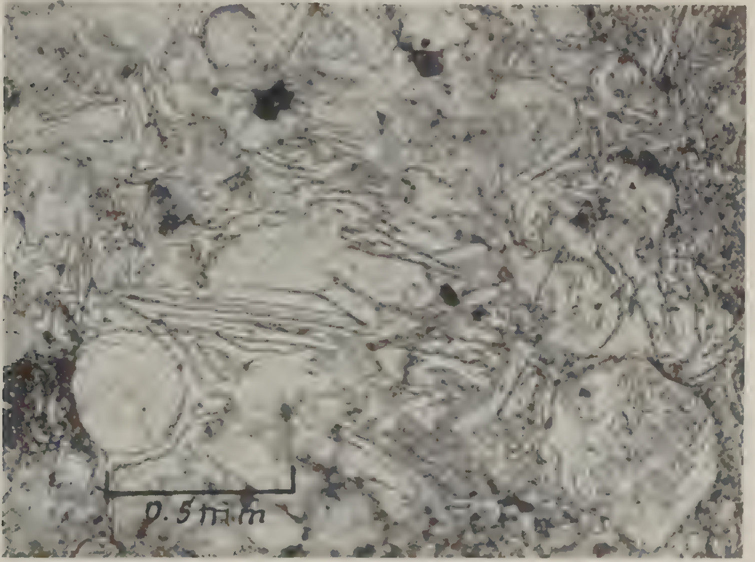

FIG. 2. Welded tuff from a deep well, Clinch County, Georgia. Rhyolitic welded tuff. The original glass of the shards has been replaced by a single unit of laumontite that covers most of the area of the figure.

The shards were originally glass, but in the upper part of the section have been replaced by laumontite, which has been identified by its x-ray and optical properties. In the lower part of the section the shards have been replaced or partly replaced by a very fine grained chertlike form of quartz.

Overlying volcanic detrital materials

The materials lying above the rhyolite welded tuff are in part made up of grains of dacite and andesite, vary greatly in size up to 4 mm. or more in diameter, and represent a fine grained volcanic conglomerate.

Thus they are not different from the materials lying below the rhyolite welded tuff. However, much of this overlying material resembles shale in the hand specimen, but microscopic examination shows that it is composed of rock and mineral grains of the order of 0.1 mm. in diameter, with much fine grained interstitial material. Rock grains similar to those of the fine grained conglomerate are present, but the proportion of feldspar is large, greatly exceeding the angular quartz grains. Thus it seems evident that an andesitic rock provided a large proportion of these mineral grains. The quartz may in part represent material derived from sedimentary rocks.

Alteration

Andesite-dacite volcanic agglomerate

The lenses characterized by andesite and dacite rock fragments were crystalline in mineral composition, in part lithic tuffs and in part devitrification products. In contrast, the rhyolite shard fragments were glassy (vitric) at the time of alteration. This difference in composition resulted in somewhat different alteration products in the conglomerate and the rhyolite tuffs and these will be discussed separately. The fine grained volcanic conglomerate lenses above and below the welded rhyolite tuff are made up of the same rock grains and do not differ in alteration products.

The order of formation of alteration products is not clear, and, possibly most of them formed at essentially the same time. The following secondary minerals associated with andesite-dacite rock debris have been identified: albite (albitized andesine), sericitic mica, epidote, pumpellyite, calcite, quartz, celandonite, saponite, chlorite, hematite, and leucoxene.

The plagioclase is clouded by minute grains of sericitic mica, and indices of refraction are in general less than 1.540. This indicates that the plagioclase has all undergone albitization, probably of andesine in the andesite, and perhaps oligoclase in the dacite. The relationships are similar to those described by Coombs (1954) in his detailed study of the alteration of volcanic tuffs in New Zealand. Like the Clinch County materials, they were dominantly volcanic in origin. In discussing plagioclase, Coombs (1954, p. 71) states, "In the vast majority of North Range rocks phenocrystic plagioclase is uniformly low-albite, composition $An_{0.4}$. Such grains are always faintly clouded and contain scattered flecks of sericite. . . there can be no doubt that such albite owes its uniform, lime-free composition to albitization of andesine. . . ." All the alteration products in the Georgia materials including the sericite seem to have developed under low-temperature conditions suggesting that the sericitic material is a hydrous mica.

Epidote in aggregates up to 0.3 mm. in diameter is abundant in some of the cores, and pale-green prisms of pumpellyite, identified optically by R. L. Smith, U. S. Geological Survey, are sporadically associated with epidote. Calcite forms irregularly shaped areas in varying proportions in all the cores. In one specimen, a fragment of limestone is included with the other rock fragments, but fragments of sedimentary rock are rare. The abundant but very small grains of leucoxene in the andesitic fragments were no doubt derived from ilmenite. Magnetite grains are sparse and magnetite seems to have been much less abundant than ilmenite in the andesitic rock. On the other hand the dacitic rock fragments contain almost no leucoxene, but do contain more dustlike magnetite than do the andesite grains. Quartz fills interstices between rock fragments and has partly replaced tuff material in the lower 10 feet of the welded rhyolite. It forms very minute grains of secondary quartz, almost resembling those of chert in some of the specimens.

The group of minerals—celadonite-saponite-chlorite—is of special interest. Celadonite, where still persisting, is recognizable by its bright-green color and high birefringence. In some specimens it is surrounded by a narrow outer film of saponite—a common relationship of these minerals. However, most of the green cavity-filling materials is now chlorite with the low birefringence and blue color at the position of extinction (strong dispersion of the axes) characteristic of many chlorites. This chlorite fills vesicular pore spaces as does typical celadonite and has the same zonal grouping of radial aggregates. The color is lighter, duller green than that of the celadonite. Some specimens show a partial alteration of celadonite to chlorite. Therefore, it seems evident that much of the chlorite was derived from celadonite. Celadonite is an iron-magnesium member of the mica group and its alteration to chlorite, in analogy with the well-known alteration of biotite, is not surprising. Chlorite also forms as fillings in the pore spaces of originally glassy pumice, as replacement material in some of the very fine grained andesitic rock grains, and as interstitial material in the very fine grained shalelike graywacke. It may have formed directly as chlorite.

Rhyolitic welded tuff

The rhyolitic welded tuffs were no doubt altered under physical conditions no different from those of the andesitic-dacitic materials; but their lower ferromagnesian content and the glassy character of the shards at the time of alteration resulted in a somewhat different relationship among the alteration products. The following alteration products have been identified in welded rhyolite tuff: saponite, celadonite, chlorite, epidote, laumontite, and quartz.

The characteristic alteration product of the rhyolite welded tuff is laumontite. In the hand specimen it is "flesh-ocher" (Ridgeway).

Coombs in his study of the aforementioned tuffs in New Zealand described laumontite, one of the important alteration products, as being buff colored. Laumontite is present in all but the basal portion of the rhyolite welded tuff that contains a large proportion of andesite and dacite rock fragments. The overlying 35 feet of tuff is all characterized by laumontite, and some horizons are almost wholly that mineral. It forms irregular areas up to 3 mm. in diameter, and so large areas of shard material are poikilitically enclosed in laumontite. In the lower part of the welded rhyolite tuff the shards have been in part replaced by very fine grained chertlike quartz, obscuring the shard structure more than has the replacement by laumontite.

The original composition of the plagioclase of the welded rhyolite tuff is problematical; but the plagioclase is now albite, and like that from andesitic rocks contains clouds of minute sericite grains. Therefore, it seems evident that it also has undergone albitization. The celadonite filling vesicular cavities with an outer rim of saponite is far less abundant than in the andesitic-dacitic tuffs, but shows the same relationships. Epidote is fairly abundant in small aggregates or in single nearly euhedral crystals.

The welding of a tuff immediately follows ash flow emplacement, and seems to have been closely followed by devitrification. Hence both processes involve heat from a magmatic source. The rhyolite tuff was emplaced by an ash flow and shows welding and therefore the question arises as to the possibility of magmatic heat contribution to the production of secondary minerals in the Clinch County well. The study by Coombs of the development of a similar group of minerals in New Zealand rocks suggests an answer to that question. The materials there had all undergone transportation and redeposition, and the only heat source considered by Coombs (1954, p. 91–93) was that resulting from depth of burial. Thus magmatic heat was not a factor in the development of the low-grade metamorphic minerals in New Zealand and this strongly suggests that the same group of minerals developed independently of magmatic heat in the Georgia materials. This conclusion would definitely include the laumontite and heulandite of the New Zealand rocks and seemingly also the laumontite of the Georgia rocks—that is, welding and devitrification and the development of low-grade metamorphic materials are entirely distinct episodes.

Regional Relationships

Volcanic rocks, including rhyolitic lavas, tuffs, basalt and volcanic agglomerates were reported from the Georgia-Florida wells discussed by Applin (1951, p. 8). These reports suggested the restudy of available materials from these wells and the restudy confirmed the earlier reports. All these materials had undergone much more alteration than those of the Clinch County well. However, the wide occurrence of volcanic agglomerate or conglomerate, probably similar to that in the Clinch County well, seems to be indicated. A core sample from Camp No. 1 well of the Sun Oil Company, Marion County, Florida, revealed well-preserved shard and pumice structures at a depth of 4,618 to 4,653 feet. The rock shows the development of zones of sericite that partly obscure the relationships, but actual welding seems to be indicated. The Jameson well No. 1, Hillsborough County, Florida, showed welded tuffs in three core samples taken between 10,010 and 10,034 feet.

The Marion County well lies about 125 miles nearly south of the Clinch County well, and that in Hillsborough County near St. Petersburg, about 200 miles south-southwest. Of course the correlation of horizons and continuity of occurrences is quite impossible with the scant information available. All we definitely know is that there is a wide occurrence of volcanic materials in the Georgia-Florida region and that welded tuffs constitute an interesting part of this wide-spread volcanism.

Geologic Age

Applin (1951, p. 11) states that, "As a working hypothesis . . . the age of these volcanic rocks is tentatively classified as early Paleozoic or possibly Precambrian." Below the volcanic rocks of the Clinch County well are several hundred feet of unmetamorphosed shalelike material, and hence it is very improbable that they are Precambrian in age. These unmetamorphosed materials suggest that the volcanic rocks of the Georgia-Florida region were laid down in early Paleozoic time as Applin strongly implies.

The andesitic and the dacitic materials were derived from rocks that were undergoing erosion, and hence represent volcanic episodes earlier than the one represented by the welded rhyolite. However, there is no indication of how much earlier. These rocks may be of essentially the same age as the rhyolitic welded tuff, or they may be Precambrian.

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THE EFFECT OF TEMPERATURE, STRUCTURAL STATE AND COMPOSITION ON THE ALBITE, PERICLINE AND ACLINE-A TWINS OF PLAGIOCLASE FELDSPARS*

J. V. Smith, *The Pennsylvania State University, University Park, Pennsylvania.*

Abstract

Donnay and Gay, respectively, have shown that the obliquity of albite twins of plagioclase feldspars varies with An-content and structural state. For sodic plagioclase and probably for intermediate plagioclase, it is now shown that the obliquity is affected much more by the temperature. Observations on the frequency of twinning in synthetic and natural plagioclase are in harmony with the theoretical frequency deduced from the estimated variation of obliquity.

In 1940, Donnay used the French geometrical theory of twinning to predict the ease of albite twinning in plagioclase crystals. In this theory, the ease of twinning is taken to be directly governed by the angular misfit of the twin components, known as the obliquity ϕ. For albite, pericline and acline-A twins the obliquity is $b \wedge b^*$ and may be calculated from the inter-axial angles by the formula $\cos\phi = \sin\alpha \sin\gamma^* \equiv \sin\gamma \sin \alpha^*$. Donnay calculated the variations of ϕ with An-content from the sparse morphological data then available and found that ϕ varied in the same way as the observed width and frequency of the albite twin lamellae. Since 1940 it has been found that plagioclase feldspars exist in various structural modifications that depend both on the An-content and the thermal history of the specimen. A by-product of these investigations has been the accurate measurement of cell dimensions and, in 1956, Gay was able to extend Donnay's work. The calculated values of ϕ, together with some new values for heated natural specimens, are shown in Fig. 1. The obliquity of plagioclases in the low structural state falls slightly from albite to oligoclase with a subsequent slow rise to anorthite. The effect of structural state on the obliquity is small and the scatter of points for specimens of the same structural state is of similar size. Nevertheless, the data of Fig. 1 show that low-albite has a higher obliquity than high-albite, the difference decreasing as the An-content increases, until near An_{20} there is a reversal of sign. In the range An_{20} to An_{50} the greater obliquity is generally given by the higher structural state though the difference is very small. For more anorthite-rich specimens the data are too sparse for conclusions to be drawn.

In this note the effect of temperature and of solid solution by potash feldspar will be discussed. MacKenzie (1952) found that the deviation

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* Contribution No. 57-8. College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

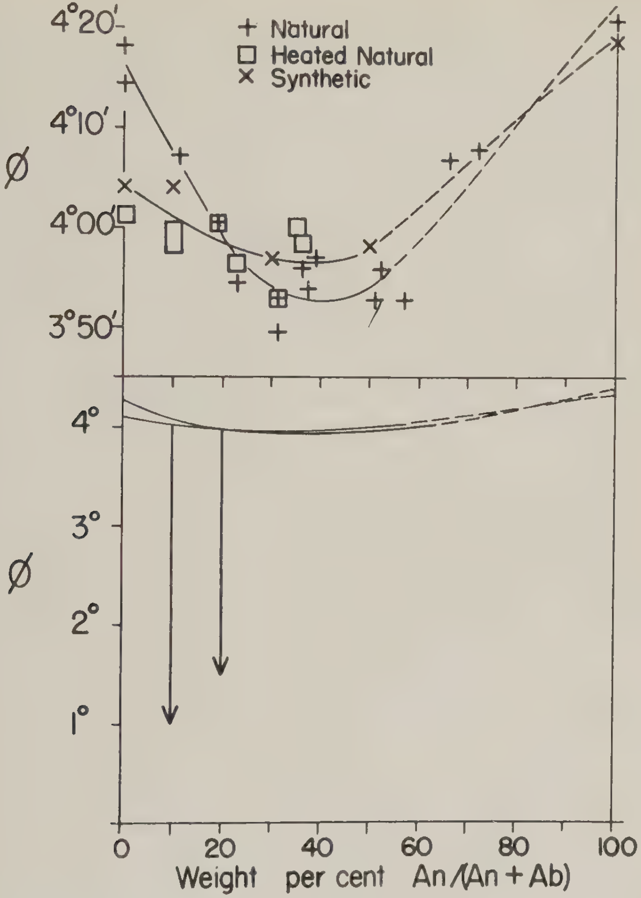

FIG. 1. The variation of obliquity with composition, structural state and temperature. The upper half of the diagram gives on an expanded scale the effect of composition and structural state at room temperature. The lower half shows on a less exaggerated scale the effect of composition and structural state, the two curves being the same as those in the upper diagram. The effect of temperature on high sodic plagioclase is indicated in a qualitative way by the arrowed lines. If the plagioclase becomes monoclinic, the obliquity becomes zero.

from monoclinic symmetry of natural and synthetic sodic feldspars decreased as the temperature was raised, until finally some of the feldspars became monoclinic. The rate of decrease depended mainly on the composition, but the method of formation and the subsequent thermal treatment had important effects. Specimens crystallized dry became monoclinic at the following temperatures: $-Ab_{95}An_5$, 960° C.; $Ab_{90}An_{10}$, 1035° C.; $Ab_{80}An_{20}$, 1380° C. Specimens crystallized hydrothermally at 800° C. and $P_{H_2O}=1000$ kg./cm.^{2} became monoclinic at the following temperatures: Ab_{100}, 1180° C.; $Ab_{90}An_{10}$, 1270° C.; measurements on specimen $Ab_{80}An_{20}$ indicated that it would become monoclinic at a temperature greater than 1500° C. Thus sodic plagioclases grown from a melt will have a zero or very small obliquity and the frequency of twinning should be high if the twinning is governed by the obliquity. Upon cooling at a rate sufficiently rapid to inhibit inversion to the low structural state, the obliquity would increase to the value calculated by Gay, but it is not likely that the lamellae would broaden. If the rate of cooling were so slow that the plagioclase inverted to the low state, it is possible that the twin lamellae would broaden, for the structural upheaval might aid a re-adjustment to the coarser lamellae theoretically required by the lower temperature. MacKenzie's results for the composition range An_0 to An_{20} show that solid solution of lime feldspar inhibits the inversion from triclinic to monoclinic symmetry. In the absence of other information these data may be extrapolated to indicate that the obliquity of structurally high andesine and more basic plagioclases falls with temperature but at a slower rate. The effect of heating on the lattice angles of low plagioclase is unknown but some qualitative studies of x-ray powder patterns by the author showed that low-albite becomes "less triclinic" as the temperature increases.

The obliquity of high-temperature sodic feldspars decreases markedly with solid solution of potash feldspar as the data obtained by Donnay and Donnay (1952) shows.

Composition	Or_0Ab_{100}	$Or_{10}Ab_{90}$	$Or_{20}Ab_{80}$	$Or_{30}Ab_{70}$
α	93.65°	93.07°	92.15°	91.31°
γ^*	87.97°	88.29°	88.61°	89.22°
ϕ	4°11′	3°34′	2°34′	1°43′

The same implication follows from the observations of Laves (1952) and MacKenzie (1952) who found that anorthoclases underwent the triclinic- monoclinic inversion at lower temperatures as the content of K-feldspar increased. Sodic plagioclases crystallized at high temperature contain up to 10–20 per cent potash feldspar in solid solution but the amount decreases sharply for the basic plagioclases. Thus for high plagioclase the effect of solid solution of potash feldspar on the obliquity may be expected to decrease rapidly with An-content. In low plagioclase the solid solution of K-feldspar is on a smaller scale and little effect on the obliquity is expected. The Or-contents of plagioclase specimens used in the construction of Fig. 1 vary from 1 to 4 per cent, but there is no recognizable correlation between the obliquity and the Or-content. Thus for practical purposes, the effect of K-feldspar on the obliquity of low plagioclase may be neglected.

From the above considerations the following deductions may be made.

(1) Plagioclase grown from a melt should be finely twinned, the frequency in volcanic specimens being somewhat higher than in plutonic specimens, for three reasons:—the temperature of crystallization is probably lower in plutonic rocks, the expected presence of water in plutonic rocks would raise the temperature of the triclinic-monoclinic inversion, and volcanic plagioclase tends to carry more potash feldspar in solid solution. In addition, the frequency of twinning in the sodic plagioclase should be higher than in calcic plagioclase because the obliquity falls more rapidly with temperature. If re-crystallization occurs in the plutonic specimens the twin lamellae may become coarser in conformity with the decreased obliquity.

(2) In metamorphic rocks twinned plagioclase should be less common than in igneous rocks, for the temperatures attained under metamorphic conditions are generally lower than in igneous bodies. With increase of metamorphic grade a transition towards igneous conditions may be expected for the obliquity falls with rising temperature. The chemical composition may be expected to play some part, but only a small part, in governing the frequency of the twinning.

These conclusions may be tested by comparison with observations recorded in the literature. Oftedahl (1948) from a study of the igneous rocks of the Oslo region in Norway found that in the volcanic rocks the twinning of the plagioclase phenocrysts was very fine, and specimens more sodic than An_{42} were optically monoclinic, indicating sub-microscopic twinning. In the plutonic rocks the twinning, although still very fine, was somewhat coarser and the boundary between the triclinic and pseudomonoclinic specimens lay at An_{30}. Van der Kaaden (1951) has also noted that in volcanic rocks the frequency of twinning varies with the An-content, the frequency decreasing markedly from oligoclase to calcic plagioclase. Tuttle and Bowen (1950) reported that albite originally in the low state developed very fine twin lamellae parallel to (010) and (001) as a result of conversion to the high structural state at temperatures near the solidus. Laves and Chaisson (1950) found that in synthetic albite the twinning was so fine that it was difficult to determine the optical properties.

In metamorphic rocks, the twinning is quite different from igneous rocks. Several quotations from Turner (1951) and Gorai (1951) are pertinent.

"(1) Prevalence of untwinned plagioclase in metamorphic rocks of all types is too well known to merit further comment. There is scattered evidence in petrographic literature suggesting that twinning of plagioclase is more frequent in rocks of moderate to high metamorphic grade than in albite-bearing schists of the greenschist facies. Thus Phillips (1930, pp. 244, 245) records increasing abundance of twinned grains of albite in passing from the chlorite zone to the biotite zone of the Scottish Daldradian schists. My own observations confirm this general tendency. . . .

(2) There seems to be no general correlation between abundance of twinning in metamorphic plagioclase and degree of deformation experienced by the enclosing rock. . . .

(3) Various writers have contrasted the simple twinning of metamorphic plagioclase with the characteristically complex twinning of plagioclase in igneous rocks. (Phillips, 1930, p. 27; Harker, 1932, p. 213). In the great majority of metamorphic rocks which I have examined, twinned grains of plagioclase consist of few subindividuals and only one twin law is represented in most grains. This contrasts very strikingly with the variety and complexity of twinning exhibited by igneous plagioclase and with the large number of lamellae that occur in many grains in igneous rocks. There are, however, certain exceptions. In pyroxene granulites, and in certain hornfelses of relatively high grade, grains of plagioclase may consist of many closely-spaced lamellae, though there is still a marked tendency for only one twin law to be represented in any grain. . . .

It seems likely that the differences noted above may reflect generally prevalent differences in the physical conditions of magmatic and metamorphic crystallization. It is possible, for example, that twinning behavior, as well as crystal habit and the nature of crystal boundaries, is affected differently by metamorphic crystallization of plagioclase in an essentially solid medium and by magmatic crystallization in a liquid medium. Temperature may well exert an even more important influence. Metamorphic temperatures in general are lower than magmatic temperatures. . . ." Turner.

"It is noteworthy, moreover, that the frequency of twinned plagioclase . . . in these metamorphic rocks (schists and gneisses of amphibolite facies) has nothing to do with the average composition of the plagioclase, but depends on the average grain size of the plagioclase in each rock" Gorai.

The general correspondence between the above observations and the predicted frequency of the twinning is clear though the comparison has been implicitly simiplified in two ways. First, it has been assumed that the frequency of twinned grains and the width of twin lamellae are directly dependent on the ease of twinning. This is not strictly true for the size and shape of the grains may also influence the nature of the twin lamellae. The influence of grain size on the frequency of untwinned grains in metamorphic plagioclase has been experimentally demonstrated by Gorai, who found, as might be expected, that there are more untwinned grains in the finer-grained schists. In spite of this complication, there can be no reasonable doubt that the twinning occurs more easily in igneous than in metamorphic plagioclase.

The second simplification has been the neglect of other twin laws. Gorai has studied in great detail the distribution of the various twin laws. He has grouped the twin laws into two classes, the A class (albite, pericline, and acline-A laws) and the C class (the other twin laws). C twins are very rare in metamorphic rocks though a few occur, especially in the higher grade rocks. In igneous rocks, C twins are more frequent, the percentage increasing with the basicity of the rock and with the An-content of the plagioclase. The complexity of twinning in igneous plagioclase is composed of two parts, the larger number of twin laws and the greater frequency of the twin lamellae. For the present purpose only the frequency of the C twin lamellae is of interest and there is little doubt that the frequency is higher in igneous than in metamorphic plagioclase.

In conclusion it should be pointed out that, while the frequency of albite and pericline twinning appears to be adequately explained in a general way by variation of the obliquity in response to changing temperature, structural state and composition, other factors are of importance. As Gay has pertinently remarked, if the obliquity provides the sole control of the twin frequency, then albite and pericline twinning should be equally developed, whereas marked disproportion between the twin laws is commonly observed. The presence of impurities, which are known to have marked effects on the habits of many crystals, may also affect the frequency of twinning. Thus the broad agreement between the twin frequency and the obliquity should not be expected to hold in all cases and genetic implications of the twin frequency should be treated with caution.

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PHYSICAL PROPERTIES AND BOND TYPE IN Mg-Al OXIDES AND SILICATES

JOHN VERHOOGEN, *University of California, Berkeley.*

ABSTRACT

From a study of physical properties that are sensitive to the electronic distribution, it is concluded that oxides and silicates of Mg and Al behave mostly as purely ionic compounds. Departures from ionic behavior are generally not such as to suggest covalent bonding.

INTRODUCTION

The solution of many petrological and geophysical problems demands an understanding of the nature of the interatomic forces in silicate minerals. The P-T range of stability of various phases, the kinetics of reactions between these phases, some of their magnetic properties, the velocity of propagation of elastic waves in the earth's mantle, its physical constitution, and its electrical conductivity, are examples of problems that involve some knowledge of the nature of interatomic forces in silicate minerals.

Of the various models that have been proposed for silicates, the ionic one, as developed by Goldschmidt, is by far the simplest. Once a set of ionic radii has been chosen, simple rules allow prediction of the coordination numbers and the general type of structure of a compound of given chemical composition. The interatomic attractive force is purely electrostatic, and the repulsive force, which arises from overlap of closed shells, contributes only a small fraction of the total lattice energy, so that its exact description is not essential to a first approximation and when dealing with phases at ordinary pressure. Goldschmidt's ionic model has unrivaled elegance and simplicity.

To be sure, not all elements and not all crystals obey the simple ionic rules. Attention has been called in recent years to an increasing number of substances for which the ionic model is inadequate (Fyfe, 1951, 1954; Goodenough and Loeb, 1954). Goldschmidt had, of course, noticed such discrepancies when he introduced into crystal chemistry the concepts of polarizability and polarizing power, both rather empirically defined. Polarization leads, in Goldschmidt's views, to a gradual transition to covalent bonding which will occur, according to him, when the polarizing power of the cations, as measured by their ionization potential, exceeds a critical value which depends on their charge and the polarizability of the anions. The present writer is not clear as to exactly what Goldschmidt's criteria may be for deciding that a compound is covalent rather than ionic; such criteria are indeed difficult to define.

An attempt to measure quantitatively the covalent character of bonds was made by Pauling by means of his well-known electronegativity scale (Pauling, 1948a). The approach is again purely empirical. It leads to assigning to Si-O, Mg-O, and Al-O, bonds slightly more ionic character than Goldschmidt would grant. The most covalent of the three, according to Pauling, is the Si-O bond, with about 50% ionic character; Goldschmidt's chart (1954, p. 105) would make it purely covalent, although he mentions on the previous page that the "ionic character is about equal in strength to the covalent bonding." The actual charge distribution was later revised when Pauling (1948b) introduced his electroneutrality principle according to which "the electron distribution in stable molecules and crystals is such that the electrical charge associated with each atom is close to zero, in all cases less than ± 1 electron." The necessary redistribution of charge is effected by formation of π bonds, which lead to a contraction of the bond length. The calculation of the Si-O distance in $(SiO_4)^{4-}$ groups now becomes an intricate affair, involving essentially empirical corrections for 1) the Shomaker-Stevenson correction (for empirical electronegativity difference) to the sum of the covalent radii; 2) the (empirical) amount of π-bond character induced by the charge distribution; 3) the (empirical) bond contraction due to π-bond formation. How much simpler it is to note that the cosine of the tetrahedral angle (109°28′) being equal to $\frac{1}{3}$, the Si-O distance is $\sqrt{\frac{3}{8}}$ times the O-O distance; thus the conventional Goldschmidt oxygen-ion radius of 1.33 leads directly to an Si-O distance of 1.63!

The truth of the matter is that a complete and exact calculation, by quantum-mechanical means, of bond energy, lattice spacing, and elastic coefficients, of any structure more complicated than the hydrogen molecule still cannot be done. Approximations must be made, and empirical procedures resorted to. What is then the *simplest* model that will account best for most properties of the substance under consideration? Surely not the covalent one, as we still cannot compute an energy of covalent bonding (except by empirical means) for molecules more complex than H_2; no one has attempted, to the writer's best knowledge, to calculate from first principles the lattice energy of diamond. The pure ionic model no doubt is the simplest; and this paper is concerned mostly in finding how well an ionic model will account for a number of physical properties of silicates and oxides of magnesium and aluminum. Because of lack of experimental data on many of the more complex silicates (e.g. pyrope), this investigation deals mainly with the component oxides SiO_2, MgO, and Al_2O_3. The remarkable additive property of the entropies (Fyfe, Turner, and Verhoogen, in press) leaves little doubt, however, that the type of bonding in the more complex oxides and silicates is essentially the same as in the component oxides.

Some of the physical properties considered, such as the diamagnetic susceptibility and the electronic polarizability, depend critically on the average radius $\bar{r}$ of the electronic distribution, $\bar{r}=\int_0^\infty r\psi^2 dv$. To compute $\bar{r}$ (or $\overline{r^2}$, or $\overline{r^3}$, as the case may be) for an ionic structure, we consider here that all electrons occupy unperturbed orbitals of the ion to which they are assigned; all the electrons in O^{2-}, for instance, are assumed to occupy unperturbed orbitals $(1s)$, $(2s)$, $(2p)$, of the oxygen atom. For a covalent structure, on the other hand, we consider again pure atomic orbitals, neglecting the concentration of charge halfway between the atoms that would normally arise from covalent bonding. As will be seen, this approximation will in general appear to favor the covalent type; that is, if the ionic model appears more adequate than the covalent one computed on this approximation, it will *a fortiori* be more adequate than the exact covalent model.

The state of oxygen in the compounds we consider appears to be particularly critical, as the ionic structure of oxides and silicates requires the presence of a doubly charged O^{--} ion which is unknown in the free state, O^- plus one electron having a lower energy than O^{--}. O^{--} may, of course, be stabilized in ionic crystal by the additional coulomb energy that accrues from its greater charge, and a quantum mechanical calculation by Yamashita and Kojima (1952) indeed seems to confirm the existence of O^{--} in alkaline-earth oxides. Some of the testing methods used in this paper place special reliance on the electronic state of the anion, which is the main contributor to electronic polarizability and diamagnetic susceptibility. Such tests are thus particularly diagnostic of the state of the crystal as a whole.

LATTICE ENERGIES

As mentioned earlier, there is no way of calculating theoretically the lattice energy of a covalent compound. By contrast, the calculation for an ionic crystal may be carried out to a high degree of precision. The main term arises from the coulomb attraction between ions, which are assumed to have a spherically symmetrical charge distribution. Small corrections may be made for dipole-dipole and dipole-quadruple interaction, and for the zero-point energy, but the sum of these generally amounts to no more than a few per cent of the total. The main uncertainty arises from the repulsive potential, which may be evaluated either from compressibility measurements or from empirical considerations; again, the repulsive term is small, and the calculated value of the energy may be within 2 or 3% of the true value. A comparison with experimental values, which are probably not accurate to more than 4 or 5%, allows a check on the validity of the fundamental assumption regarding the ionic character of the substance.

A list of calculated and experimental values may be found in the Landolt-Bornstein Tables (1950), volume I, part 4, pp. 539–543. It appears from these lists, as is well known, that the agreement for the alkali halides, even CsI, is excellent; so is it for the oxides of the divalent elements and corundum. The diagnostic value of the method suffers, however, from the fact that the agreement is also quite good for sphalerite, wurtzite, galena, and other sulfides which one would hesitate, on other grounds, to call ionic. It is interesting that the lattice energy of substances that may not be purely ionic may apparently also be computed as if they were.

The following values (Table I), taken from the L.B. Tables, illustrate the general agreement for oxides.

TABLE I. LATTICE ENERGY
(Kcal/mole)

	Calculated	Experimental
BeO	1080	1053
MgO	936	913
CaO	830	823
Al_2O_3	3720	3609

CAUCHY RELATIONS

It is well known that if the lattice structure is such that every atom or ion occupies a center of symmetry, and if the particles interact with forces that depend only on distance (central forces), the following relations must exist among the elastic constants (Born and Huang, 1954, p. 136).

$$C_{23} = C_{44} \qquad C_{31} = C_{55} \qquad C_{12} = C_{61}$$

$$C_{14} = C_{56} \qquad C_{25} = C_{46} \qquad C_{36} = C_{45}$$

These relations are known as the Cauchy relations; they reduce the number of independent elastic constants in the general case from 21 to 15. In crystal with symmetry higher than triclinic, some of the Cauchy relations are identically satisfied, as the corresponding elastic constants are equal to zero. Thus, in hexagonal and rhombohedral crystals the Cauchy relations reduce to

$$C_{13} = C_{44}$$

$$C_{11} = 3\,C_{12}$$

regardless of whether there are, 5, 6, or 7 independent elastic constants. In cubic crystals, there is a single Cauchy relation

$$C_{12} = C_{44}$$

between the 3 independent elastic constants.

In crystals consisting of spherically symmetrical ions, forces should be central; in crystals held together by covalent bonds they should not. Thus the Cauchy relations could be used to test the ionic vs. covalent character of a compound, provided it fulfills the additional requirement that each particle should occupy a center of symmetry. This latter requirement rules out, for instance, corundum, but applies to any crystal with NaCl structure. NaCl itself, for which $C_{12}=1.30\ 10^{12}$ dynes/cm.^{2}, $C_{44}=1.278\times10^{12}$ dynes/cm.^{2} at 270° K. (Durand, 1936), seems indeed to satisfy the Cauchy relations; MgO, however, does not, as shown by the following figures (Durand, 1936).

T° K	C_{11}	C_{12} (10^{12} *dynes/cm.*^{2})	C_{44}
80	29.87	8.56	15.673
300	28.93	8.77	15.477
560	27.25	8.96	15.092

Failures of the Cauchy relations in ionic crystals have been assigned to a number of causes. Herpin (1953) believes that they arise from the polarizability of the ions. Löwdin (1956) has shown by a thorough quantum-mechanical treatment of the alkali halides that a notable fraction of the lattice energy arises from many-body potentials. The forces acting between two ions depend on the presence or absence of other ions in the neighborhood, and are therefore not purely central, i.e., function of only the separation between the ions. Laval (1957) and his collaborators have insisted that the introduction of non-central forces must, in fact, invalidate the classical theory of the elasticity of crystals; there should be, in the general case of non-central forces in a triclinic crystal, 45 rather than 21 independent static elastic constants.

Whatever the case may be, it should be noted that very few substances, if any, satisfy the Cauchy relations. The agreement for NaCl mentioned above is really fortuitous, as the temperature coefficients of C_{12} and C_{44} have opposite signs (see Hearmon, 1956). Thus the Cauchy relations offer no test of whether a crystal is ionic or not; what they test is whether the ions are deformable or not. In addition, Löwdin has shown quantitatively for NaCl that the difference between C_{12} and C_{44} arises almost entirely from the repulsive term in the expression for the potential energy of the crystal; this repulsive term, in turn, is only a fraction of the total energy. Thus the existence of many-body potentials will only slightly affect the cohesive energy, which, as we know, comes out correctly on the ionic hypothesis. Stated in other words, elastic constants being second derivatives of the potential energy, one might obtain a potential energy function which would not yield the correct elastic constants but which would still give usable results with regard to the cohesive energy and the volume.

X-RAY METHODS

If one now looks for physical properties that depend on the actual distribution of electrons in the crystal, the atomic scattering factor f first comes to mind. This factor, which is the ratio of the radiation amplitude scattered by the charge distribution in an actual atom to the amplitude scattered by a point electron at the center, is

$$f = \int_0^\infty U(r) \frac{\sin \mu r}{\mu r} dr$$

where $U(r)$ is the radial electronic density and $\mu = 4\pi \sin\theta/\lambda$, λ being the wave length of the radiation, and θ the angle between the direction of the incident radiation and the scattering plane. One notes that for $\theta = O$, $f = Z$, the total number of electrons in the atom. Thus, if one could measure f for various values of θ at fixed λ, extrapolation of the experimental curve to $\theta = O$ would indicate whether the atom is ionized, and to what degree. Atomic scattering factors have been calculated for many atoms and ions from the charge distribution computed by various methods (Hartree's self-consistent field, Thomas-Fermi, etc.); these calculations generally show that the scattering factors for an atom and the corresponding ions differ appreciably only at small values of μ, as shown in Table II for aluminum.

TABLE II. ATOMIC SCATTERING FACTOR OF ALUMINUM AND ALUMINUM IONS*

	Sin $\theta/\lambda \times 10^{-8}$			
	0.0	0.1	0.2	0.3
Al^{3+}	10.0	9.7	8.9	7.8
Al^{2+}	11.0	10.3	9.0	7.75
Al^{+}	12.0	10.9	9.0	7.75
Al	13.0	11.0	8.95	7.75

* Hartree, with interpolation for Al^{+} by James and Brindley. L. B. Tables, vol. I, part 1, p. 300.

The Landolt-Bornstein Tables (vol. I, part 1, pp. 300 310, 1950) give an extensive list of references on the experimental values of scattering factors; these may then be compared with theoretical values to determine the actual charge on the atom. The experimental determinations require that due allowance be made for thermal vibrations, which depend on the temperature and the compound of the atom being studied. Various other necessary corrections, as for extinction, were not made in early work. We note the value of f for oxygen in Fe_3O_4 at $\sin\theta/\lambda = 0.07$, which is 9.3 (Claasen, 1926); this implies a negative charge greater than that of

O^-, for which $f=9.0$ at $\theta=O$. Froman (1930) found the total number of electrons on oxygen in MgO to be 9.3, the corresponding number for Mg in the same substance being 10.32. Wyckoff and Armstrong (1930) also determined the scattering factors for oxygen and magnesium in MgO, but only for values of $\sin \theta/\lambda$ which do not allow a discrimination between the various possible electronic states. For the values for MgO determined by Brill, Hermann, and Peters, see below.

Essentially the same information that goes into the determination of the scattering factor may be used for a Fourier analysis, which gives in a more graphic form a representation of the electron density distribution in a crystal. By integration of the density outward from an atomic position to a radius where the electronic density is negligible, the total charge on an ion in the crystal may be computed. Several investigators, using this method, agree that the total charge on Na in NaCl is close to 10.05 electrons, that on Cl being about 17.85 (Witte, 1956; Brill, 1939; Havighurst, 1927); this corresponds to about 90% ionic character, which is considerably more than the Pauling electronegativity scale would allow. Brill *et al.* (1939) find a density of only 0.006 electrons/Å^3 at positions $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Brill, Hermann, and Peters (1948) have also examined MgO; they find a distribution that is less localized than in NaCl, the density in MgO nowhere being less than 0.15–0.2 electrons/Å^3. There is, however, no indication of directional bonding: the density at the same distance is about the same in the [100] and [110] directions. This is in contrast with diamond, in which there is a strong charge concentration on lines joining the atoms, with corresponding low electronic densities at other points. The atomic scattering factors, corrected for temperature, are listed in Table III, together with the theoretical factors from the Hartree-James-Brindley Tables.

The experimental scattering factors listed in Table III are not inconsistent with a purely ionic structure. Brill, Hermann, and Peters (1948) concluded, however, from a more detailed study of the electronic density distribution, that a certain amount of covalent bonding must be present. The density distribution is indeed interesting: going out from an atomic position the density at first drops sharply in all directions, then tails off to a fairly uniform value. This occurs at about 0.9 Å from the center of a magnesium position along the [111] and [110] directions, and at about 1.15 Å from the center of the oxygen position along these same directions. Only in the [100] direction is there a sharp minimum ($0.3e/\text{Å}^3$) at about 1.0 Å from Mg and 1.1 Å from O. The ions thus both seem to be very nearly spherical, although magnesium seems larger, and oxygen smaller, than their conventional ionic radii would predict. Along the [111] direction one finds a zone, about 1.6 Å in length, along which the density has an almost constant value of $0.15–0.20e/\text{Å}^3$.

Table III. Experimental Scattering Factors in MgO,* and Theoretical Values†

Sin θ/λ	Mg exp.	Mg^{++}	Mg	O exp.	O^{--}	O^{-}	O
0	—	10.0	12.0	—	10.0	9.0	8.0
0.1	(9.5)	9.75	10.5	(8.0)	8.0	7.75	7.1
0.2	8.24	8.6	8.6	5.76	5.5	5.65	5.3
0.3	7.06	7.25	7.25	4.02	3.8	3.95	3.9
0.4	5.78	5.95	5.95	2.87	2.7	3.0	2.9
0.5	4.65	4.8	4.8	2.25	2.1	2.3	2.2
1.0	2.02	2.0	2.0	1.36	1.35	1.35	1.35

* Brill, Hermann, and Peters, 1948.

† L. B. Tables, vol. I, part 1, p. 300. Values for Mg^{++} and O do not agree well with recent calculations by Berghuis *et al.* (1955).

In Table IV are listed some electronic densities computed either from the approximate Slater wave functions (see for instance Coulson, 1952, p. 40) or, when available, from the density distribution curves in the Landolt-Bornstein Tables, vol. I, part 1, pp. 284 ff.; the latter curves are plotted from a variety of sources, most of which use the method of Hartree's self-consistent field.

The last entry in the table is the computed density midway between oxygen and magnesium, assuming a double covalent bond of the type $\psi=\psi_0(2p_x)+\psi_{\mathrm{Mg}}(3s)$, the bond length being taken as 2.1 Å. The $(2s)$ and $(2p)$ orbitals of Mg, and the $(2s)$ and remaining $(2p)$ orbitals of oxygen are assumed to be undisturbed.

The observed density of 0.3 between Mg and O along the cube edge is seen from Table IV to be consistent with a superposition of the densities of Mg^{++} and O^{--}; it is much less than the covalent value 0.63. The den-

Table IV. Typical Electronic Densities

Atom or ion	Distance from center of atom (Angstrom units)	Electronic density (electrons/Å^3)	Source
Mg^{++}	0.85	0.13	L.B. Tables
O	1.06	0.16	L.B. Tables
	1.27	0.06	L.B. Tables
	1.9	<0.004	L.B. Tables
O^{-}	1.06	0.2	L.B. Tables
	1.27	0.09	L.B. Tables
	1.9	0.008	L.B. Tables
O^{--}	1.06	0.27	Calculated from Slater function
	1.85	0.002	Calculated from Slater function
Mg–O covalent	1.05	0.63	See below

sity of about 0.2 at 1.15 Å from oxygen along the face and body diagonals is again about correct for an undisturbed O^{--} ion, but the diffuse and even distribution between ions of opposite sign along the body diagonal, and between ions of the same sign along the face diagonal, cannot be reconciled with a simple ionic model nor, for that matter, with any simple covalent model. As Brill, Hermann, and Peters point out, the situation is somewhat reminiscent of the distribution in metals. The total number of electrons on Mg and O, out to a given distance, is given in Table VII.

Too much weight should not be given to these figures, as they must embody the fundamental uncertainties inherent in the type of analysis: clearly, one cannot expect much detail or precision on the scale of 0.1 Å when using radiation with a wave length many times larger. One derives, however, the rather surprising result that in MgO the net charge on Mg is probably somewhat larger than 2, while that on O is somewhat less than 2. The structure is thus not a simple ionic one, but deviations are not of the type expected in covalent bonding. In particular, the spherically symmetrical distribution of charge around the nuclei, the absence of any localized bonds such as found in diamond, and the appreciable, but smooth and uniform electron density over a large fraction of the cell suggest more a transition to a metallic state than to a covalent one.

To the writer's best knowledge, no detailed studies of this kind have been made on any other oxide of the element under consideration. One notes with interest that Parker and Whitehouse (1932) found a full complement of 26 electrons on Fe in pyrite (FeS_2), and that Witte (1956) finds indications of electron concentration between Li and F in LiF, making this substance somewhat less ionic than NaCl.

DIAMAGNETIC SUSCEPTIBILITY

An electron moving within an atom is equivalent to a tiny current in a resistanceless conductor. When an external magnetic field is applied through an electrical circuit, an induced current is set up, the magnetic effects of which tend to oppose the primary field. In the same way the electronic motion within an atom will be disturbed by an applied magnetic field in a way such as would be equivalent to a current tending to cancel the applied field. This effect leads to diamagnetism, which exists in all substances, although it may be overshadowed by more powerful effects of the opposite sign in paramagnetic or ferromagnetic materials. It can be shown (e.g., Kittel, 1953, pp. 134–135; Selwood, 1956, chap. V) that the diamagnetic susceptibility for unit volume χ_v is given by the simple Langevin expression

$$\chi_v = -\frac{Ze^2N}{6mc^2}\overline{r^2} \tag{1}$$

where N is the number of atoms per unit volume, Z the number of electrons per atom, e and m, respectively, the charge and mass of the electron, c the velocity of light, and r^2 is the mean square distance of an electron from the center of the atom. Instead of χ_v one also uses the molar susceptibility χ_M, which is equal to χV, V being the molar volume, and the specific susceptibility, or susceptibility for unit mass, $\chi_d = \chi_M / M$, M being the molecular weight. Substituting numerical values of fundamental constants in (1), one finds

$$\chi_M = -\, 2.82\ 10^{10} \sum \overline{r^2}$$

where the summation is to be extended over all the electrons in each atom. If radial distances are expressed in atomic units ($a_0 = 0.528 \times 10^{-8}$ cm.), we get

$$\chi_M = -\, 0.79\ 10^{-6} \sum \overline{r^2}.$$

Thus the diamagnetic susceptibility depends essentially on the radial distribution of electrons around the nuclei, which would be different in covalent and ionic structures. If one compares, for instance, the structures Mg-O and Mg^{++}-O^{--}, the 2 electrons transferred from Mg to O will occupy on the oxygen ion orbitals of smaller average radius than that of the ($3s$) electrons of the isolated magnesium atom. As the effect of a covalent bond is generally to concentrate charges between the bound atoms, the change from the covalent to the ionic structure should be accompanied by a notable decrease in susceptibility. A comparison of calculated and observed values of χ will thus give information regarding the actual state in the crystal. One notes that, in general, the larger anions will contribute more to the susceptibility than the smaller cations.

Formula (1) is strictly valid only if the charge distribution is spherically symmetrical. For diatomic and other non-symmetrical molecules, one must add a term of opposite sign which represents a paramagnetic contribution (Van Vleck paramagnetism) differing from ordinary paramagnetism due to uncompensated spins in that it is temperature independent. Theoretically the Van Vleck term should vanish only in completely symmetrical systems in which the field direction is an axis of symmetry and the electronic distribution is spherically symmetrical about the nuclei; it is difficult to evaluate exactly and is not likely to be important in crystals of high symmetry.

For an electron with wave function ψ, it follows from the definition of $\overline{r^2}$ that

$$\overline{r^2} = \int_0^\infty r^2 \psi^2 dv$$

and may therefore be calculated if the wave function ψ is known. A particularly simple formula can be obtained for $\overline{r^2}$ if one uses Slater wave functions of the type

$$\psi = Ar^{n-1}e^{-cr/n}$$

where A is a normalizing factor, n is the principal quantum number of the electron, and c, the effective charge, is equal to the atomic number Z minus the screening constant s which is computed according to Slater's well-known rules (see, for instance, Slater, 1951, p. 476). A simple integration yields directly

$$\overline{r^2} = n^2(n + \tfrac{1}{2})(n + 1)/c^2. \tag{2}$$

Pauling (1927), by a more elaborate calculation, finds

$$\chi = -2.01 \times 10^{-6} \sum \frac{n^4}{(Z - s)^2}\left[1 - \frac{3l(l + 1) - 1}{5n^2}\right] \tag{3}$$

where l is the second quantum number of the electron. Pauling gives in tabulated form the susceptibilities of many common ions. For O^{--}, for instance, he finds $\chi_M = -12.6 \times 10^{-6}$, whereas the simpler Slater formula (2) gives -12.8×10^{-6}. Susceptibilities have also been calculated from various other models and are collected in the Landolt-Bornstein Tables (vol. I, part 1, pp. 394 ff.). A calculation using the Thomas-Fermi-Dirac model has recently been made by Thomas and Umeda (1956).

Experimental susceptibilities of ions have been obtained from measurements on solutions and crystals. It appears that ionic susceptibilities are nearly additive; for example, the difference between the molar susceptibilities of LiF and NaF is nearly the same as the difference between LiCl and NaCl. The matter is reviewed by Selwood (1956), who gives (p. 78) an extensive table of ionic susceptibilities.

The diamagnetic susceptibility of minerals is difficult to measure, because of paramagnetic impurities (e.g., Fe^{++} or Fe^{+++}) which may overshadow the diamagnetic effects, even when these impurities are present only in very small amounts. Surprisingly, there is even some uncertainty regarding the susceptibility of common oxides. Yamashita and Kojima (1952), while studying the electronic state of O^{--} in MgO, used a value of -18.8×10^{-6} for the molar susceptibility of this oxide; there are, however, several other determinations which give an average value of -10.5×10^{-6} (Ray, 1955). The International Critical Tables (vol 6) gives on page 359 a value of -10.2 (in units of 10^{-6}) for Al_2O_3, and on page 364 a value of -34.7; the latter value will be used here, as it agrees with measurements of Rao and Leela (1953) on white sapphire. Corundum is slightly anisotropic, and the value given here is an average. Spinel ($MgAl_2O_4$) is listed in I.C.T. as paramagnetic ($\chi_M = +88 \times 10^{-6}$) which seems unlikely in the absence of iron or manganese impurities.

The following table (Table V) shows the molar diamagnetic suscepti-

TABLE V. MOLAR DIAMAGNETIC SUSCEPTIBILITIES (IN UNITS OF -1×10^6)

	O	O^{--}	Mg	Mg^{++}	Al	Al^{3+}	Si	Si^{4+}	C^{4+}	C	C^{4-}
Pauling	—	12.6	—	3.2	—	2.5	—	2.1	0.15	—	50.0
Slater	7.0	12.8	27.5	3.1	26.9	2.5	25	2.0	—	7.4	—

bility of several ions and atoms computed by Pauling (1927) or by Slater's formula (2).

From these values one obtains by simple addition the following values (all multiplied by -1×10^6), which may be compared with listed experimental values (Table VI).

The figures for diamond show that the diamagnetic susceptibility of a covalent crystal is not very different from that computed by addition of atomic susceptibilities; we note that the susceptibility per atom of diamond is greater than that of a single carbon atom, in keeping with the expected effect of covalent bonding mentioned above. By contrast, the figures suggest a truly ionic state for SiO_2. For Al_2O_3 the agreement between the experimental susceptibility and the sum of the susceptibilities of the ions is still fairly good; clearly, the state of Al_2O_3 is more ionic than covalent. The figures for MgO require closer scrutiny.

Yamashita and Kojima (1952) have examined the stability of the O^{--} ion in oxide crystals. Using Hartree-Fock wave functions for Mg^{++} and (1s) and (2s) electrons of O^{--}, they determine by a variational method the parameters of an empirical wave equation for (2p) electrons that will minimize the energy of the crystal for an Mg-O distance of 2.1 Å. Repeating the procedure for O^{-}, they find that O^{--} is decidedly more stable (by about 12 e.v.) than O^{-} in magnesium oxide. They also compute the ionic susceptibilities which they find to be -3.7×10^{-6} for Mg^{++} and -21.0×10^{-6} for O^{--}, in this same compound. This would make the molar susceptibility of MgO (-24.7×10^{-6}) much too large in absolute value.

Essentially the same result would accrue from the electron density distribution of Brill, Hermann, and Peters discussed above. It will be recalled that the main features of this distribution are: 1) an unusually

TABLE VI. CALCULATED AND EXPERIMENTAL* SUSCEPTIBILITIES, FOR VARIOUS STRUCTURES (IN UNITS OF -1×10^{-6})

MgO			Al_2O_3			SiO_2			C^1 (diamond)		
Mg–O	Mg^{++}–O^{--}	exp.	Al–O	Al^{3+}–O^{--}	exp.	Si O	Si^{4+}–O^{--}	exp.	C–C	C^{4+}–C^{4-}	exp.
34.5	15.9	10.5	74.8	43.55	34	39	27.6	25.6	14.8	50.15	12.0

* Value for MgO from Ray (1955); others from International Critical Tables.

large magnesium ion, extending outward to 0.9-1 Å; 2) a very high and uniform density between the oxygen and magnesium; this density being almost as large as that (0.3 electron/A^3) of the conduction electrons in Al (Witte, 1956); and 3) a somewhat small oxygen ion. If the diffuse charge is assigned to any one of the ions, its spatial extension becomes so large that its diamagnetic susceptibility, which is proportional to $\bar{r^2}$, becomes enormously greater than the experimental value.

The following table (Table VII) gives the total number of electrons and the corresponding ionic susceptibilities computed by integration of the density data of Brill, et al., out to a specified distance. From this table we see that if we assume, for instance, radii of 0.9 for Mg and 1.2 for oxygen, the total number of electrons on the ions is 9.2+8.6=17.8, leaving 2.2 electrons per ion pair in the inter-ionic space; the sum of the susceptibilities of Mg and O comes out as 15.5, which again is more than the experimental value. From this we infer that a small paramagnetic susceptibility must also be present. This paramagnetic contribution is considerably smaller than the Pauli paramagnetism of interstitial electrons with a density of 0.2/Å^3; these should anyhow form a filled band and could not be regarded as "free," as the extremely low intrinsic conductivity of MgO clearly shows. Similarly, the paramagnetism due to a single uncompensated electron spin, as would occur in ions such as O^- or Mg^+, would be of the order of 10^{-3} rather than 10^{-6} at ordinary temperature. Thus presumably the small paramagnetic contribution must be a Van Vleck term, arising from the fact that the field at the center of the cube forming $\frac{1}{8}$ of the unit cell is far from symmetrical; indeed, on any body diagonal of this elementary cube there are ions of *opposite* signs on either side of the side.

TABLE VII

Mg			O		
1 Radius (Å)	2 Total number of electrons	3 Diamagnetic susceptibility	4 Radius	5 Total number of electrons	6 Diamagnetic susceptibility
0.9	9.2	5.8	1.15	8.3	9.0
1.0	9.6	6.9	1.20	8.6	9.7
			1.33	9.0	10.9
			1.40	9.3	11.9

Summing up, the diamagnetic susceptibility of SiO_2 is consistent with that calculated for a purely ionic structure. The agreement between measured and calculated values for an ionic model of Al_2O_3 is not very good, and it is bad for MgO. In the latter compound, there is probably a small paramagnetic component arising from a high electronic density in regions of the unit cell where the field is not centro-symmetric. Departures between measured and "ionic" susceptibilities are definitely not suggestive of covalent bonding, the ionic values being intermediate between experimental and covalent ones.

POLARIZABILITY

When a dielectric substance ("insulator") is subjected to an electrical field E, charges within the substance may be displaced. Now displacing a charge $+e$ by a distance x is equivalent to adding a charge $(-e)$ at the original position and a charge $+e$ at the new position; this, in effect, is equivalent to adding a dipole ex in the direction of the displacement. If the polarization P is defined as the vector sum of the induced dipoles per unit volume, the displacement vector D is defined as $D=E+4\pi P$, and the dielectric constant ϵ, which is the ratio of D to E, is given by the relation

$$\epsilon = 1 + 4\pi \frac{P}{E} = 1 + 4\pi\kappa \tag{4}$$

where $\kappa = P/E$ is the electrical susceptibility.

Consider an atom of type i in a crystal, and assume that under the effect of the electrical field E_{loc} acting on it, it acquires a dipole moment p_i. The polarizability α_i of this atom is then defined as $\alpha_i = p_i/E_{\mathrm{loc}}$ and

$$P = \sum_i E_{\mathrm{loc}} N_i \alpha_i \tag{5}$$

where N_i is the number of atoms of type i per unit volume. If one further defines $\alpha = \sum_i n_i \alpha_i$, where n_i is the number of atoms i per molecule, one may write

$$P = N \frac{\alpha}{V} E_{\mathrm{loc}} \tag{6}$$

where V is the molar volume and N is Avogadro's number.

E_{loc} is the effective field acting on an atom inside the solid. If one sets simply $E_{\mathrm{loc}} = E$, one gets the well-known Drude formula

$$\epsilon - 1 = 4\pi \frac{N}{V} \alpha.$$

In general, however, the field at any point inside the crystal is the sum of the external field E and contributions arising from the polarization of neighboring atoms. The calculation of E_{loc} is complicated, except in cases where the distribution of atoms is isotropic, or where the lattice has a high degree of symmetry* (see Kittel, p. 92). One finds then

$$E_{\text{loc}} = E + \frac{4}{3}\pi P \qquad (8$$

from which derives the well-known Clausius-Mosotti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi\frac{N}{V}\alpha. \qquad (9)$$

A more general expression used by Mott and Gurney is

$$E_{\text{loc}} = E + \frac{4}{3}\pi\gamma P \qquad (10)$$

where γ is an empirical factor to be determined from experiments.

We must now consider two separate effects. When the field has a very high frequency, as in the visible part of the spectrum, the dielectric constant in media of unit magnetic permeability is equal to the square of the index of refraction; accordingly, from (9) we get

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi\frac{N}{V}\alpha \qquad (11)$$

a relation known as the Lorentz-Lorenz equation from which α may be determined. This value of α is called the "optical," or "electronic" polarizability, as the polarization arises entirely from shifts in the distribution of the electron clouds with respect to the positively charged nuclei. At lower frequencies, as in the infrared, an additional effect arises from the relative displacement of the positive and negative ions in the crystal. This additional contribution to the dielectric constant is said to arise from "atomic" or "ionic" polarizability. In purely covalent crystals, such as diamond, there is no ionic polarizability, as the atoms carry no net charge; accordingly their dielectric constant in low-frequency or static fields is equal to the square of the index of refraction corrected for dispersion. A comparison of the index of refraction, suitably extrapolated to zero frequency, with the dielectric constant in static fields affords thus a measure of the ionic character of the substance.

We consider first the electronic polarizability.

ELECTRONIC POLARIZABILITY

From (11) it follows that α has the dimensions of a volume; indeed one would expect the deformability of an atom to be proportional to its spatial extension. A theoretical calculation of the polarizability is easy for simple atoms, such as hydrogen: all that has to be done is to add to the potential energy of the electron arising from the coulomb attraction to the nucleus the energy arising from the external field. A simplified quantum-mechanical calculation (Pitzer, 1953, p. 69) leads to the approximate value for hydrogen $\alpha = 4a_0^3$, where a_0, the "radius" of the hydrogen atom, is $0.528\ 10^{-8}$ cm. A correct calculation (Pauling and Wilson, 1935, pp. 227–229) yields $\alpha = 9/2a_0^3$. More generally, the electronic polarizability will be a function of $\overline{r^3}$, the mean cube radius of the electronic density distribution, just as the diamagnetic susceptibility measures the mean square radius. It is historically interesting that the first determination of the radius of the O^{--} ion was made precisely from a consideration of polarizability.

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* More precisely, the condition is that the coordinates $x_iy_iz_i$ of the lattice points around a central lattice point taken as the origin should satisfy the condition that $\sum(r_i^2) = 3\sum(z_i^2)$, where $r_i^2 = x_i^2 + y_i^2 + z_i^2$. This condition is satisfied if $x_i^2 = y_i^2 = z_i^2$.

Pauling (1927) suggested that the polarizability of an atom should be given by the relation

$$\alpha = 0.281 \sum_{0}^{ln} \frac{(5n^6 + 7n^4)(2l + 1)}{(Z - \sigma_{nl})^4}$$

where n and l are the two first quantum numbers of an electron, σ_{nl} is an appropriate screening factor, the summation being carried over all electrons in the atom. Slater (1951, p. 204) points out that as the radius of an orbit with quantum number n is roughly proportional to $n^2/(Z-s)$, where Z and s are, as usual, the charge on the nucleus and the Slater screening factor, the polarizability should be proportional to

$$\left(\frac{n^2a_0}{Z - s}\right)^3;$$

the proportionality factor would be 4.5 for $n=1$, 1.1 for $n=2$, 0.63 for $n=3$, etc. The Slater rule is somewhat easier to apply than the Pauling formula.

The value for hydrogen ($9/2\ a_0^3$) cannot be checked because of the absence of measurements on *atomic* hydrogen. For the helium atom, the experimental value of α is 0.205×10^{-24} cm.^{3}. Pauling and Wilson (1935, pp. 226–229) calculate values ranging from 0.15 to 0.23 Å^3, depending on the choice of wave function. The Slater rule gives $\alpha = 0.27$ Å^3. Further comparisons are listed in Table VIII.

We note the very small polarizability of the smaller cations, as compared with that of large anions.

Polarizability of ions in solution and certain crystals obey an additivity law similar to that followed by ionic diamagnetic susceptibilities. Tables of empirical polarizabilities have been set up in this way (see Kittel, 1953, p. 97).

In Table IX are listed the values of the polarizability of several compounds, computed by adding the Slater values of the polarizability

TABLE VIII. COMPARISON OF THE POLARIZABILITY OF VARIOUS IONS CALCULATED BY PAULING (1927) AND BY THE SLATER RULE

	Polarizability of ions, in Å³,	
	According to Pauling (1927)	Calculated by Slater rule
O^{--}	3.88	1.46
Be^{++}	0.008	0.026
Mg^{++}	0.094	0.17
Al^{3+}	0.052	0.12
Si^{4+}	0.0165	0.08

of the component ions. These values may be compared with the experimental values

$$\alpha = \frac{3V}{4\pi N} \frac{n^2 - 1}{n^2 + 2},$$

n being the index of refraction for the sodium D line, or an arithmetic mean of the indices for non-cubic crystals.

The agreement between figures in the two columns is surprisingly good, when it is remembered that the Lorentz-Lorenz formula (11) is strictly applicable only to substances with high symmetry, and that the Slater rule is only approximate as it neglects the difference between orbitals of same principal quantum number but different l. Where disagreement exists is it not an indication of strong covalent bonding, as the following values (Table X) for covalent vs. ionic structures show.

TABLE IX. COMPARISON OF POLARIZABILITIES OF VARIOUS COMPOUNDS, DERIVED FROM INDICES OF REFRACTION OR CALCULATED BY ADDITION OF POLARIZABILITIES OF IONS

	Polarizability of compounds (in units of 10^{-24} cm.³)	
	$\alpha = \frac{3V}{4\pi N} \frac{n^2-1}{n^2+1}$	$\alpha = \Sigma\, n_1\alpha_1$ (Calculated by Slater rule)
BeO	1.31	1.49
MgO	1.75	1.63
Al_2O_3	4.18	4.62
$MgAl_2O_4$	6.2	6.25
SiO_2 (quartz)	2.86	3.00
SiO_2 (cristobalite)	2.90	3.00
$BeAl_2O_4$	5.65	6.11
Mg_2SiO_4	6.45	6.26
$MgSiO_3$	4.72	4.63

TABLE X. CALCULATED AND EXPERIMENTAL POLARIZABILITY OF MgO AND BeO

	Polarizability (10^{-24} cm.^{3})	
	Calculated	Experimental
$Mg+O$	6.83	1.75
$Mg^{+}+O^{-}$	3.30	
$Mg^{++}+O^{--}$	1.63	
$Be+O$	3.50	1.31
$Be^{+}+O^{-}$	1.86	
$Be^{++}+O^{--}$	1.49	

Strictly speaking, the polarizability of a covalent compound need not be equal to the sum of the polarizabilities of its constituents; the correction for covalency is, however, small, as shown by diamond: the polarizability of the isolated carbon atom, computed by the Slater rule, is 1.2×10^{-24} cm.^{3}; the experimental value for diamond is 0.84×10^{-24}.

As the polarizabilities of the cations are small and not likely to be much in error, we have computed the value of the polarizability of the oxygen that would give perfect agreement with experimental data. Results are as follows:

TABLE XI. POLARIZABILITY OF THE OXYGEN ION IN VARIOUS COMPOUNDS

MgO	1.58×10^{-24}
Mg_2SiO_4	1.51
$BeAl_2O_4$	1.50
$MgSiO_3$	1.49
$MgAl_2O_4$	1.45
SiO_2 (quartz)	1.39
SiO_2 (cristobalite)	1.41
Al_2O_3	1.31
BeO	1.28
$CaCO_3$	1.31
Al_2SiO_5 (sillimanite)	1.40
Al_2SiO_5 (andalusite)	1.39
Al_2SiO_5 (kyanite)	1.34
$Mg_3Al_2Si_3O_{12}$ (pyrope)	1.39
Average	1.41

The average of these 14 values, 1.41, is very close to the value for O^{--} obtained by the Slater rule (1.46). It is interesting that the cube root of the polarizability, which might be taken as an empirical radius, is 1.16 A for O in MgO; this is precisely the distance at which the electron density around the O sites tails off. Similarly for $CaCO_3$: the empirical radius of $\sqrt[3]{1.31}=1.1$ is that which one would compute from the C-O distance (1.27 Å) assuming that the 3 oxygens surrounding carbon are just touching.

The electronic polarizability of an ion, as we have seen, is a function of the average radius of the electronic density; it should therefore be closely related to the ionic radius itself. We thus expect a relationship between the index of refraction of a compound and the radii of its constituent ions. Kordes (1956) has found empirically a relationship of this type. The "optical" ionic radii computed by him from refractive indices agree well with the conventional ionic radii, corrected where necessary for coordination number. He finds no indication of covalent bonding either in SiO_2 or in grossularite ($Ca_3Al_2Si_3O_{12}$).

In summary, the polarizability of compounds computed by adding the polarizabilities of their ions agrees with experimental values, if one uses the Slater rules to determine the polarizability of the ions. Polarizability gives no clear evidence of covalent bonding in any of the compounds considered.

IONIC POLARIZATION

Consider a substance consisting of positive and negative ions. Under the influence of an external electrical field, the positive and negative ions will be displaced in opposite directions; these displacements produce a polarization which contributes to the dielectric constant an amount which is proportional to the net charges on the ions and to their displacement. These displacements, in turn, depend on the restoring forces between ions; if one assumes, for instance, a restoring force $f=Kx$ proportional to the displacement x, x will be given by the simple relation $Ee=Kx$ where e is the charge on the ion, E the field acting on it, and K is the force constant. The induced dipole is ex, and the polarizability $\alpha=ex/E=e^2/K$.

Now if the restoring force between two particles of mass m_1, m_2 is proportional to the displacement, the particles will oscillate with a frequency

$$\omega_0 = \sqrt{K/\mu}$$

where μ is the reduced mass

$$\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}.$$

This frequency usually falls in the infrared. In the visible part of the spectrum the frequency of the electric field is much greater than the natural frequency of oscillation of the ions which remain essentially undisturbed; the ionic polarization does not contribute to the dielectric constant or to the index of refraction, which arises entirely from the electronic polarizability discussed above. For a static electric field, or in general for fields with frequency less than ω_0, the oscillations of the ions contribute a polarization which increases the dielectric constant. The dielectric constant for static fields is thus found to be greater than n^2 by an amount $\Delta\epsilon$, n^2 being the square of the refractive index extrapolated to infinite wave length by a suitable dispersion formula. $\Delta\epsilon$ thus measures the charge on the ions and the force constant. As the force constant also determines the compressibility, one expects a relation between the actual charge on the ions, the compressibility, $\Delta\epsilon$, and the fundamental frequency ω_0. Thus if $\Delta\epsilon$ and ω_0 or the compressibility are known, it should be possible to determine the actual charge on the ions. Conversely, one could also compute the compressibility for purely ionic structures and compare the calculated and experimental values.

There is an abundant literature on the subject (Højendahl, 1938; Szigeti, 1949, 1950; Mott and Gurney, 1948, pp. 20–21; Kittel, 1953, pp. 98–100; Born and Huang, 1954, chap. II). Difficulties arise from a correct evaluation of E_{loc}, the field acting on a particle inside the structure. It was pointed out earlier that both the Drude formula ($E_{\text{loc}}=E$) and the Lorentz-Lorenz formula ($E_{\text{loc}}=E+4/3\ \pi P$) are approximate. The field is not necessarily homogeneous and need not be the same at various points within an ion of finite size. The ionic polarization also affects the electronic polarization, and the ions may overlap and thus become deformed. As mentioned before, Mott and Gurney use the more general relation (10) $E_{\text{loc}}=E+\gamma 4/3\ \pi P$ where γ is an empirical factor to be determined from the dielectric constant and compressibility; they find rather good agreement for alkali halides if $\gamma=0$; but they believe that difficulties in estimating γ preclude accurate calculation of the dielectric constant or of the exact charge distribution; they point out that homopolar bonding will increase the dielectric constant, and recall that the high dielectric constant of rutile (about 100) and other salts has been ascribed to an effect of this type; of which more later.

Szigeti (1949) recognized that the polarizability should depend on the wave length and character of the wave (whether longitudinal or transverse); the Lorentz-Lorenz formula (11) should hold for the polarizablity of a sphere in long waves, whereas the Drude formula (7) should be applicable to short transverse waves. Taking into account possible overlap of ions, and the interdependence of electronic and ionic polarizabilities, Szigeti derived a relation between $\Delta\epsilon$, n, the frequency of the transverse optical branch and the effective charge sze on the ion, where z is the valency and e the charge of one electron. Values of s for alkali halides range from 0.69 (for KI) to 0.93 (for NaF); s is usually somewhat larger than the ionic character obtained from Pauling's curve, but does not vary systematically with the Pauling electronegativity scale: for instance, KI and RbI should have the same amount of ionic character according to Pauling, whereas s is 0.69 for KI but 0.89 for RbI. One is surprised to find $s=1$ for CuBr, and $s=1.10$ for CuCl. Szigeti obtains $s=0.88$ for MgO, taking the wave length of the fundamental infrared absorption band to be 17.3 μ; if one uses Saksena's (1956) value 25.2 μ, s comes out at 0.62, although the agreement between calculated and measured compressibility is much improved.

It seems difficult to ascertain whether Szigeti's results bear significantly on the matter of ionic vs. covalent bonding. Szigeti believes that the deviation of s from the value unity is caused mainly by the mutual distortion of neighboring ions owing to their overlap; this is independent of, and need not reflect on, the total number of electrons on the ion.

The view was expressed above that homopolar binding might tend to increase the dielectric constant, and that the high dielectric constant of compounds such as rutile has to be ascribed to this effect. Other explanations are also possible. Szigeti finds $s=0.7$ for rutile, which implies a notably ionic structure. The Clausius-Mosotti equation, which is based on the Lorentz field $E_{\mathrm{loc}}=E+4/3\ \pi P$, may be rewritten

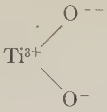
$$\epsilon = \frac{1+\dfrac{8\pi}{3}\dfrac{N}{V}\alpha}{1-\dfrac{4\pi}{3}\dfrac{N}{V}\alpha}$$

which shows that ϵ may be very large if

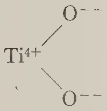
$$\frac{4\pi}{3}\frac{N}{V}\alpha$$

happens to be sufficiently close to 1. For static or low frequency fields, α must of course include the ionic and electronic polarizabilities.

The electronic polarizability of rutile is interesting: from the average value of the index of refraction (2.705), one finds $\alpha=5.1\times10^{-24}$ cm^3. The polarizability of Ti^{4+} is small (0.19 according to Pauling; 0.45 according to the Slater formula), so that the polarizability of O^{--} should be 2.3×10^{-24} or more, which is much greater than in the other oxides considered so far. It is actually not necessary to resort to covalent bonding to account for the anomaly if one notices that the ionization potentials of $3d$ and $4s$ electrons in titanium are almost equal; thus the Ti^{+3} ion would have a large polarizability due to its remaining ($4s$) electron, and a small admixture of the ionic state



to the state



would appreciably increase the electronic polarizability.

In conclusion, it would appear once again that there is nothing in the theory of electronic or ionic polarizability that compels us to abandon a simple ionic representation of the compounds presently under consideration.

Coordination Numbers

In covalent bonds the coordination number of an atom depends essentially on the ease with which it can form hybrid orbitals of various types. On the other hand, the coordination number of a cation is predictable, in the purely ionic model, by the simple radius-ratio rule: the number of nearest neighbors depends solely on the ratio of the ionic radii of the anion and cation. According to this rule, one generally expects to find small cations in a lower coordination than large ones. At first sight, the structure of spinel ($MgAl_2O_4$) in which Mg is in 4-coordination and Al in 6-coordination, appears anomalous. There has been a tendency to explain such anomalies in radius-ratio rules by recourse to covalent bonding. As it turns out, the structure of any particular member of the spinel group can be simply explained in terms of an ordinary coulomb attraction between charged ions, the Madelung constant being larger for the normal than for the inverse structure for large values of the oxygen parameter u (Gorter, 1954). One could argue, however, that the tendency of any particular ion to occupy 4-coordinated (A) sites rather than 6-coordinated (B) sites, or vice versa, determines in the first place whether the structure will be normal or inverse, the oxygen parameter u then adjusting itself so as to minimize the coulomb energy. It is thus interesting to compute the energy that would be necessary to transfer any particular ion from, say, a 6-coordinated (B) site to a 4-coordinated (A) site of the spinel structure. X-ray, crystallographic, and magnetic data are fortunately available from which the distribution of the various ions among the A and B sites may be calculated in minerals and artificial "ferrites" with the spinel structure. Consider the general case of a spinel with formula $MN_{2-t}Q_tO_4$ in which M is a divalent element (Mg, Ni, Fe^{2+}, etc.), while N and Q are trivalent elements (Al, Fe^{3+}, etc.). Assume the distribution to be

$$M_xN_yQ_z[M_{1-x}N_{2-t-y}Q_{t-z}]O_4$$

where brackets indicate 6-coordinated cations in B sites, and $x+y+z=1$. The configurational entropy is $S=K\ ln\ W$ where K is Boltzmann's constant and

$$W = \frac{1!(2-t)!t!}{x!y!z!(1-x)!(2-t-y)!(t-2)!}.$$

If U is the internal energy and F the Helmholtz free energy $F=U-TS$, a simple algebraic calculation yields

$$\begin{aligned}\frac{\partial F}{\partial x} &= U_x' - KT\ ln\frac{1-x}{x}\\ \frac{\partial F}{\partial y} &= U_y' - KT\ ln\frac{2-t-y}{y}\\ \frac{\partial F}{\partial z} &= U_z' - KT\ ln\frac{t-z}{z}\end{aligned} \tag{12}$$

when $U_x'=\delta U/\delta x$, etc. Since $x+y+z=1$, F is minimum when

$$\frac{\partial F}{\partial x} = \frac{\partial F}{\partial y} = \frac{\partial F}{\partial z}$$

so that in the equilibrium configuration we have (Smart, 1954)

$$\begin{aligned}U_x' - U_y' &= KT\ ln\frac{(1-x)y}{x(2-t-y)}\\ U_y' - U_z' &= KT\ ln\frac{(2-t-y)z}{(t-z)y}\\ U_z' - U_x' &= KT\ ln\frac{(t-z)x}{(1-x)z}.\end{aligned} \tag{13}$$

In these relations, $U_x'-U_y'$ is the energy necessary to move an atom of M from a B to an A site, an atom of N being simultaneously transferred from an A to a B site. These energy differences may thus be calculated from measured values of x, y and z. Note that only differences such as $U_x'-U_y'$ can be gotten in this way; the values of U_x', U_y', U_z' can be obtained separately only on the assumption that enough vacancies exist in A and B sites that the relation $x+y+z=1$ need not hold; that is, that one could transfer an atom from a B to an A site without simultaneously moving another atom from A to B.

A carefully studied compound of this type is $MgFe^{3+}O_4$, with structure $Mg_xFe_y^{3+}[Mg_{1-x}Fe_{2-y}^{3+}]O_4$, for which x has been determined as a function of temperature by Pauthenet and Bochirol (1951) (see also Bertaut, 1951). For a binary compound, equations (13) simply reduce to

$$U_x' - U_y' = KT\ ln\frac{(1-x)^2}{x(x+1)}. \tag{14}$$

The calculated values vary slightly with temperature, due perhaps to incomplete annealing at lower temperature; at high temperature (1200° C.) the authors find $U_x' - U_y' = 0.11$ e.v. A calculation based on the assumption stated above gives

$$U_x' = +0.15 \text{ e.v.} = 3500 \text{ cal/mole}$$
$$U_y' = +0.04 \text{ e.v.}$$

only the difference between these two quantities being truly significant.

Similar calculations have been carried out for other compounds and are listed in Table XII. Data are from Gorter (1954); Greenwald, Pickart and Grannis (1954); Bacon and Roberts (1953). In all the instances listed, it has been assumed that measured values of x, y, and z are those for specimens perfectly quenched from a high temperature (1200° C.). This may not be generally true, as some workers used annealed specimens; some of the energies listed in Table XII may thus be too large by a factor of 2 or 3.

TABLE XII. ENERGIES (IN ELECTRON VOLTS) TO TRANSFER ATOMS FROM 6- TO 4-COORDINATES SITES IN SPINELS

Compound and distribution	U'_{Mg}	U'_{Ni}	$U'_{Fe^{3+}}$	U'_{Al}	Transfer energies
$Mg_{0.22}Fe_{0.78}^{3+}[Mg_{0.78}Fe^{3+}_{1.22}]O_4$	+0.15		+0.04		$U'_{Mg} - U'_{Fe} = 0.11$
$Mg_{0.53}Fe^{3+}_{0.47}[Mg_{0.47}AlFe^{3+}_{0.52}]O_4$	−0.015		+0.015		$U'_{Mg} - U'_{Fe} = -0.03$
$Fe^{3+}_{0.96}Al_{0.04}[Fe^{2+}Al_{0.16}Fe^{3+}_{0.84}]O_4$			−0.015	+0.18	$U'_{Fe^{3+}} - U'_{Al} = -0.19$
$Ni_{0.16}Fe^{3+}_{0.24}Al_{0.61}[Ni_{0.85}Fe^{3+}_{0.01}Al_{1.14}]O_4$		+0.221	−0.41	+0.1	$U'_{Fe^{3+}} - U'_{Al} = -0.51$
$Ni_{0.05}Fe^{3+}_{0.68}Al_{0.27}[Ni_{0.95}Fe^{3+}_{0.32}Al_{0.73}]O_4$		+0.375	−0.1	+0.12	$U'_{Fe^{3+}} - U'_{Al} = -0.22$

The energies listed in Table XII, as explained, are approximate; yet their magnitude is very striking in being so small. Compare, for instance, the promotion energies of aluminum to a valence state sp^3 (tetragonal hybrid; 3.6 e.v.) or to a d state (octahedral hybrid; 7.5 e.v.). Clearly, the equilibrium distribution of ions among the 4- and 6-coordinated positions in the spinel structure depends on very small energy differences that do not suggest any fundamental difference in type of binding. The transfer energy for a given pair (e.g., Al-Fe^{3+}) also varies appreciably as a function of composition, or of cell dimensions. The general trend for Mg is to go into A sites only when the structure is such that the radii of the A and B sites are nearly equal; when the radius of a B site becomes appreciably (20%) larger than that of an A site, the transfer energy of Mg becomes positive, as in $MgFe_2O_4$. Aluminum has precisely the opposite tendency, its transfer energy becoming more and more positive as the ratio r_6/r_4 becomes smaller. In $MgAl_2O_4$, $r_6 = r_4$; accordingly Al is in B sites and Mg in A sites. Such relationships are not easily explainable in terms of purely covalent binding.

It would seem to follow from these considerations that a departure from the usual coordination number (e.g., Mg in 4- rather than 6-coordination) does not necessarily imply an appreciable change in the amount of covalent bonding; simple electrostatic considerations may still be used to predict coordination numbers in the spinel structure.

It is interesting to note that Loeb and Goodenough (1955), who rely on covalent bonding to explain a number of structural features of spinels, consider that Mg and Al in spinels are essentially electrovalent, in agreement with our conclusion. Covalent effects occur only with transition or heavier elements.

It is unfortunate that so few data should be available on the physical and thermochemical properties of the aluminum silicates Al_2SiO_5, in which the aluminum coordination is either 6 (kyanite), or 6 and 5 (andalusite), or 6 and 4 (sillimanite). As far as is known, it would seem that the free energies of these three compounds do not differ by more than a few thousand, or even perhaps a few hundred, calories at room temperature and ordinary pressure. The entropy of any of these 3 phases is almost exactly the sum of the entropies of the oxides, corrected for density differences. The polarizability of the oxygen ion (Table XI) is the same in sillimanite and andalusite; in kyanite it is exactly equal to the average for quartz and corundum. Here again, it seems unlikely that the change in coordination should reflect any notable change in electronic density distribution and bond type.

This does not mean that coordination numbers cannot, in some rare instances, be taken to indicate the presence of a notable amount of covalent bonding. ZnO is a good example. Surely, as has been pointed out many times, the difference between MgO (6-coordination, NaCl structure) and ZnO (4-coordination, wurtzite structure) cannot be explained on the basis of radius-ratio considerations, as Mg^{++} and Zn^{++} are said to have rather similar radii. However, tetrahedral coordination presumably requires hybridization, the ease of which may be roughly evaluated by comparing the ionization potentials of successive electron shells or subshells. For instance, the difference in ionization potential of $2p$ and $2s$ electrons in C is 0.7 atomic units (1 atomic unit $= 13.54$ e.v.); $3p-3s$ in silicon is 0.5; $4s-3d$ in Zn is 0.5; etc. By contrast, consider $3s-2p$ in Mg $=3.1$, $4s-3p$ in Ca $=1.45$. Thus one expects hybridization, and formation of tetrahedral coordination, to occur readily in C, Si, Zn, but not in Mg, Ca, etc. It is interesting that ZnO and BeO are actually the only oxides of bivalent elements that occur in either the zincblende or wurtzite structures; and the 4-coordination of Be in BeO is readily explained on radius-ratio considerations alone (radius of $Be^{++}=0.35$). In the same way, one expects on general grounds that carbon would occur covalently either in 2-(CO_2) or 4-coordination (CH_4). The occurrence of the CO_3 group in carbonates is difficult to explain (Fyfe, 1954); yet it follows directly from radius-ratio rules.

SUMMARY AND CONCLUSIONS

We have examined such physical properties of simple oxides and silicates of Mg and Al as could lead, independently of any chemical considerations, to an evaluation of the ionic or covalent character of these compounds. We noticed first that *lattice energies* computed for purely ionic structures usually agree well with "experimental" values, as they also do for some sulfides and selenides with less pronounced ionic characteristics. The *Cauchy relations* between elastic coefficients offer no critical test of ionicity; they point to the existence of non-central forces which may arise from a mutual deformation of ions rather than from directed bonds of covalent type. *X-ray data* on MgO are interesting: they show the presence of nearly perfectly spherical units, with a charge distribution suggesting a structure intermediate between Mg^{++} -O^{--} and Mg^{++} —O^{-}, the remaining electrons are spread out evenly without any indication of localized bonds. The interpretation of the *diamagnetic susceptibility* offers some difficulty. Experimental determinations are few and likely to be inaccurate because of the presence of uncontrolled amounts of paramagnetic impurities. Results for SiO_2 are quite consistent with a fully ionic structure Si^{4+}—O^{--}, and the same applies, to a lesser degree, to Al_2O_3. For MgO the susceptibility suggests a structure more ionic than Mg^{++}—O^{--}, and one suspects an appreciable Van Vleck term related to the interstitial electrons mentioned above. The *electronic polarizability* is again consistent with a fully ionic structure, the average polarizability of oxygen in a number of compounds being almost exactly that predicted by the Slater rule for O^{--}. The *ionic* polarizability shows departures from the values expected for purely ionic structures, although differences may be due in large part to theoretical difficulties in evaluating the internal field; the degree of covalency derived from the ionic polarizability does not agree with that calculated from the electronegativity values. *Coordination numbers* are probably rather poor indicators of covalent vs. ionic character. The calculated values of the *transfer energy* required to interchange 6-coordinated and 4-coordinated cations in spinels turn out to be so small as to suggest very little difference in bond character in the two sites.

Thus it would seem that on the whole, the physical properties of the compounds studied are much more easily explained on ionic than on a covalent basis. This is, surprisingly, particularly true of SiO_2, which is generally regarded as at least 50% covalent. The agreement between experimental data and values calculated for purely ionic structures is by no means perfect; but the fault may reside in the theory. There is, of course, ample evidence that ions do not behave as rigid spheres; they are deformable, as the index of refraction readily shows. This polarizability, however, seems calculable on a purely electrostatic theory and is therefore more amenable to treatment than when interpreted in terms of covalent binding. The polarizability will lead to difficulties in estimating elastic coefficients, but would not seem to be of major importance in other calculations.

We conclude, therefore, that for practical purposes it is legitimate to consider the compounds under consideration as purely ionic.

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A CHALCEDONY-LIKE VARIETY OF GERMANIA

J. F. White, E. R. Shaw and J. F. Corwin,* *Departments of Chemistry and Geology, Antioch College, Yellow Springs, Ohio.*

Abstract

A fibrous variety of GeO_2 (quartz type) was produced hydrothermally. It has anamolous physical and optical properties which are analogous to the corresponding form of silica, chalcedony. Accordingly, this variety may be termed chalcedonic germania.

Refractive indices determined for single crystals of GeO_2 (quartz type) are slightly different from those previously reported.

Introduction

During hydrothermal studies in the system GeO_2—H_2O, single crystals of GeO_2, analogous to quartz, were produced under certain conditions. With a slight variation in conditions, a fibrous modification with distinct optical and physical properties was formed, and is subsequently referred to as chalcedonic germania.

To prepare the quartz-type crystals of GeO_2, germanium dioxide glass, in the form of irregular lumps of about 0.5 gram each, was reacted at 200° C. and 12 atmospheres with 5 ml. of distilled and demineralized water. In runs of about 2 hours, the glass was converted *in situ* to the hexagonal form as shown by optical examination and *x*-ray powder patterns. However, this is a metastable form. GeO_2 (rutile type) is the low temperature form according to Laubengayer and Morton (1932), with a transformation to the hexagonal form at about 1033° C. Apparently at 200° C. in the presence of water, GeO_2 glass first reacts to give the metastable hexagonal form. With runs at higher temperatures or for longer periods, the product was invariably the rutile-type of GeO_2.

The optically and physically distinct chalcedonic modification was produced by the same methods, except that the autoclave was rapidly cooled by quenching with water.

GeO_2 (Quartz Type)

The hexagonal crystals of GeO_2 were identified by the *x*-ray powder diffraction data in the ASTM card file, and gave the same pattern as the chalcedonic germania.

The refractive indices reported in the literature by Laubengayer and

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Morton (1932) need revision. Careful measurements were made by the immersion method using sodium light and temperature corrections with calibrated liquids. The birefringence was also determined, using a Berek compensator. A summary of the morphological and optical properties is given in Table 1.

CHALCEDONIC GERMANIA

The following observations show chalcedonic germania has anomalous properties in relation to the quartz form. Further, these properties are very similar and comparable to those of the chalcedonic form of silica.

As shown in Fig. 1, the chalcedonic germania looks like a hemispherical variety of ordinary chalcedony. It consists of microscopic, fibrous, fan-shaped aggregates; the larger aggregates being about 0.1 mm. in size. Although the fibrous character is marked, individual fibers are so narrow that they are difficult to distinguish. In orientation, the fibers range from approximate parallelism to strongly divergent groups. Under crossed nicols, most of the fibers show approximate straight extinction, but some have extinction angles ranging from small up to about 30°. Also, some of the fiber groups exhibit wavy or varying extinction in different places along their length. Almost all of the fibers or fiber groups are length-slow, but a few are length-fast. In addition, traces of concentric banding are occasionally present. In color, much of the germanium chalcedony appears distinctly brown in transmitted light in contrast to the colorless appearance of the quartz form of GeO_2. However, the color is gradational, and the fibrous aggregates vary, often along the length of the fiber bundles, from a distinct brown to colorless. All of the above mentioned properties appear to be the same or highly similar to those found in chalcedony.

TABLE 1. MORPHOLOGICAL AND OPTICAL DATA ON GeO_2 (QUARTZ-TYPE)

Habit (A) Rhombohedrons, approximately cubes.
(B) Equally developed + and − rhombohedrons (geometric hexagonal dipyramids) with hexagonal prism

Uniaxial, optic sign +	Previously reported
$\omega=1.697\pm0.001$	$\omega=1.695$
$\epsilon=1.724\pm0.003$	$\epsilon=1.735$
Birefringence 0.027 ± 0.002	$B=0.040$
Length slow (+elongation)	

The refractive indices of germania chalcedony are compared in Table 2 to the quartz-type of GeO_2 and also to the refractive indices of the cor-

TABLE 2. REFRACTIVE INDICES OF QUARTZ AND CHALCEDONY AND THE CORRESPONDING VARIETIES OF GeO_2

Chalcedony	Chalcedonic germania
1.533–1.539 1.530	1.653 1.633
Quartz $\omega=1.544$ $\epsilon=1.553$	Quartz type of GeO_2 $\omega=1.697$ $\epsilon=1.724$

responding silica varieties as given by Winchell (1951). The refractive indices of chalcedonic germania are variable as are those of chalcedony, and those given in Table 2 refer to the more chalcedonic material. Actually, refractive indices of some of the fan-shaped aggregates range from

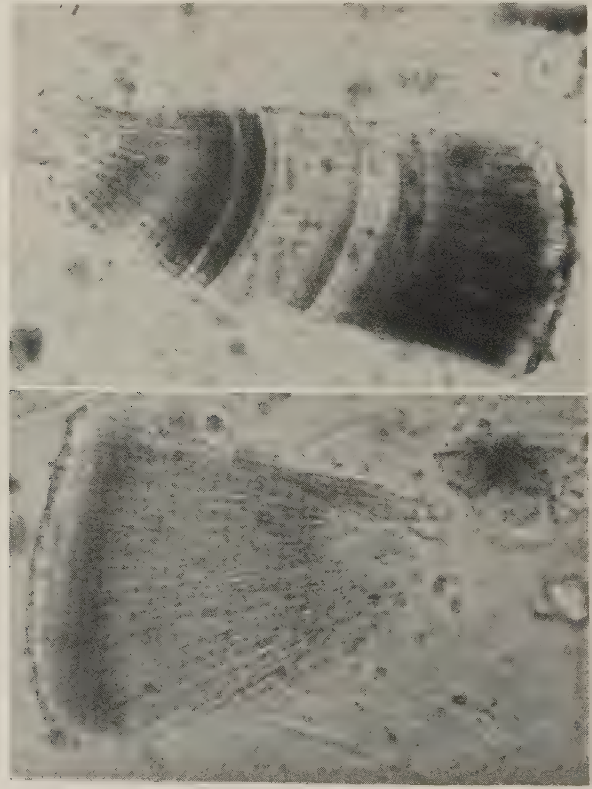

Fig. 1. Chalcedonic germania showing banding (above) and fibrous texture. Ordinary light. Magnification 600×.

those given for the chalcedonic variety up to those of the quartz type. This change appears to be gradational along the length of some of the fibrous aggregates. Corresponding with gradational changes in refractive indices, there is a gradational change in color from a distinct brown for the chalcedonic material of lowest refractive indices to colorless for the quartz form. In the case of chalcedony Folk and Weaver (1952), by using the electron microscope, showed that small cavities are present and that these produce a brownish color in transmitted light. Refractive index and specific gravity were also shown to vary in proportion to the abundance of the holes. According to Pelto (1956), the brown color is due to the preferential scattering of blue light by suitably small submicroscopic pores. Thus, the brown color of germanium chalcedony which is associated with low refractive indices, along with variation toward lighter color with higher refractive indices, supports the idea that the anomalous properties of germanium chalcedony are also due to the presence of submicroscopic holes.

The specific gravity could not be accurately measured because of the presence of small amounts of the quartz form and the variable nature of some of the material. However, a reliable estimate can probably be calculated by the use of refractive indices and chemical composition in the same manner as has recently been emphasized to give reliable densities for minerals by Jaffe (1956) and Allen (1956). Using the Gladstone-Dale relation, the specific refractivity of GeO_2 was calculated as .165 from refractive indices measured on the quartz form and x-ray density. Using this specific refractivity and refractive indices, the calculated specific gravity of the germanium chalcedony referred to in Table 2 is 3.9 and compares to 4.28 for the quartz type.

The chalcedonic germania was identified structurally by x-ray powder pattern and derived unit cell measurements which are compared in Table 3 to those given by Donnay and Nowacki in Crystal Data, 1954. In addition, infrared absorption spectra in the range 2–15 microns, which were obtained for both the quartz and chalcedony forms, gave essentially identical and characteristic patterns except for minor differences in intensities.

TABLE 3. COMPARISON OF UNIT CELL MEASUREMENTS

Chalcedonic germania	Quartz type GeO_2 (from Crystal Data)
Hexagonal $a_0=4.96$ Å $c_0=5.65$	Hexagonal $a_0=4.972\pm.005\ kX$ $c_0=5.648\pm.005$

In summary, the properties of chalcedonic germania are very similar and comparable to those given for chalcedony: Winchell (1951), Rogers and Kerr (1942), Folk and Weaver (1952), and Pelto (1956). Chalcedonic germania is essentially a fibrous variety of the quartz form of GeO_2 with anomalous physical and optical properties. There is thus the common problem of anomalous properties of the chalcedonic forms of GeO_2 and SiO_2. Chalcedony, according to Pelto (1956), is regarded by recent workers as microcrystalline quartz with submicroscopic pores containing water; while earlier workers supported the idea of interstitial, amorphous silica. In the present investigation, the gradational relationship between the chalcedonic and quartz varieties, as well as the relation between refractive indices and color, support the concept that the chalcedonic varieties are quartz forms with submicroscopic holes.

ACKNOWLEDGMENTS

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MORINITE FROM THE BLACK HILLS

D. JEROME FISHER, *University of Chicago, Chicago, Illinois*
AND
J. J. RUNNER, *University of Iowa, Iowa City.*

ABSTRACT

Unit cell, space group, morphology, optical and other physical properties of the rare pegmatite monoclinic phosphate mineral morinite from the Hugo Mine, Keystone, S. Dakota, are given. Crystallochemical similarities and differences with epidote are described. Associated minerals are montebrasite, apatite, augelite, wardite, and probably crandallite, as well as quartz and a clay mineral; paragenetic relations are briefly discussed.

In 1933–34 Runner obtained the samples which form the subject of this study from a mineral stand in Keystone, S. Dakota, run by the daughter of E. E. Hesnard (see Landes, 1929). She was certain that her father had collected them from the Hugo mine, but could supply no other information. Runner was unable to find the mineral suite in place.

Runner identified the minerals on the basis of the data shown in Table 1. Fisher verified the augelite, morinite, and wardite by means of x-ray powder patterns. The "primary" mineral of the suite is hydroxian amblygonite (montebrasite), which occurs as coarsely cleavable white masses, part of a typical "nodule." This is embayed and apparently partially replaced by massive cleavable medium-fine grained light gray augelite; vugs in this are lined with the typical tabular subhedra of this mineral (3 by 1 mm.). Crossing the massive augelite in various directions are bundles of nearly parallel crystals of prismatic apatite up to an inch or more in length; these have a coarsely fibrous appearance. Some of this fibrous apatite is a deep violet color, but this grades off (along a single crystal) to light gray material with locally a bluish cast. In Runner's thin-sections he has noted fibrous apatite (frequently violet) cutting amblygonite, and augelite.

In one specimen, outside of the centimeter-wide band of augelite-fibrous apatite (which extends about half way around a projecting knob of amblygonite), there is a somewhat wider zone consisting of faintly pinkish (nearly colorless) morinite crystals in masses of light greenish to light bluish apatite. The morinite is massive, coarsely crystalline, and only locally shows a fair cleavage surface; it has a slightly oily luster, and striated crystal faces up to a centimeter long may be observed. The apatite also has an oily luster, is massive, coarse-grained and shows fair cleavage surfaces up to a centimeter across; it is probably subhedral, but this is not readily evident. No criteria to tell the relative ages of these two minerals were noted. However they are quite possibly younger than the augelite.

One specimen carrying the fibrous apatite has a small vug lined with

TABLE 1. OBSERVED PROPERTIES OF MINERALS

	Apatite	Augelite	Crandallite	Montebrasite	Morinite	Wardite
Color	Blue-grn. to violet	Cols.		White	Cols. to pale pink	Cols.
Habit	Prismatic	Tab. xtals, granular	Tiny prisms	Massive, cleavable	Prismatic, striated	Pyr. xtals, granular
Cleavage	Good, basal	Perfect prismatic	Perfect, ⊥to elong.	3; 1 perf., 1 good, 1 dist.	1 good, ‖elong.	1 good (basal)
H	5	4½	—	6	4½	—
G	—	—	—	2.85	2.962	—
α	1.628	1.573	1.620+	1.613	1.551	1.589
β	—	1.575	—	1.624	1.563+	1.589+
γ	1.632	1.588	1.630−	1.638	1.565	1.599
2V	0°	47°		75°+5°	43°	0°-5°
Sign	(−)	(+)	+elong.	(+)	(−)	(+)
Disp.		—		$r<v$ weak	$r<v$ weak	—
B.B.	Fusibility high	Swells, whitens, barely fusible		Fuses easily	Swells, whitens, barely fuses	
c.t.	H_2O	H_2O			H_2O	

NOTE. Optical properties were found with white light using certified immersion liquids, corrected for temperature: 2V determinations based on Mallard's constant.

Qualitative chemical tests were carried out on all minerals except crandallite and wardite. All tests made showed the normal elements to be present. In addition, the morinite gave a weak Li flame and is partially soluble in hot HCl and HNO_3. The apatite yielded a positive test for OH and F, negative ones for Cl and Mn

striated euhedra (1 mm.) of colorless wardite that appears to be dipyramidal. This and other vugs have fine hexagonal needles of white silky apatite crossing them, obviously a late mineral. Massive semi-milky quartz occurs in one sample, associated with amblygonite and the massive greenish apatite. Crandallite (?) and a clay mineral were observed locally in tiny veinlets in the amblygonite. It is interesting to note the absence of feldspar, micas, beryl, and columbite in these specimens.

Morinite was described by Lacroix from Montebras, France in 1891; its analysis by Carnot was first given in 1908. Ježekite (pronounced yĕ′ zhĕ-kīt) was described by Slavik from Greifenstein near Ehrenfriedersdorf, Saxony in 1914. In 1947 Frondel (Pabef, II, 784) established that a fragment labelled morinite from Montebras supplied to him by Slavik was identical with ježekite. Volborth in 1954 at Viitaniemi, Finland, found samples of relatively massive morinite which were penetrated by needles of ježekite (see his photo 31). What he called ježekite was based on scanty data; for instance, he was unable to separate it from the morinite, thus no *x*-ray diffraction pattern was obtained. Moreover the optical properties used by Volborth to distinguish these two minerals are too closely similar to be significant of anything except minor differences in chemical composition; thus ježekite may be regarded as a sodian hydroxian morinite. *X*-ray powder patterns taken by the writer of Volborth's morinite, Greifenstein ježekite and the Black Hills sample, are identical; see Fig. 1. Spacings and indices are given in Table 2; the

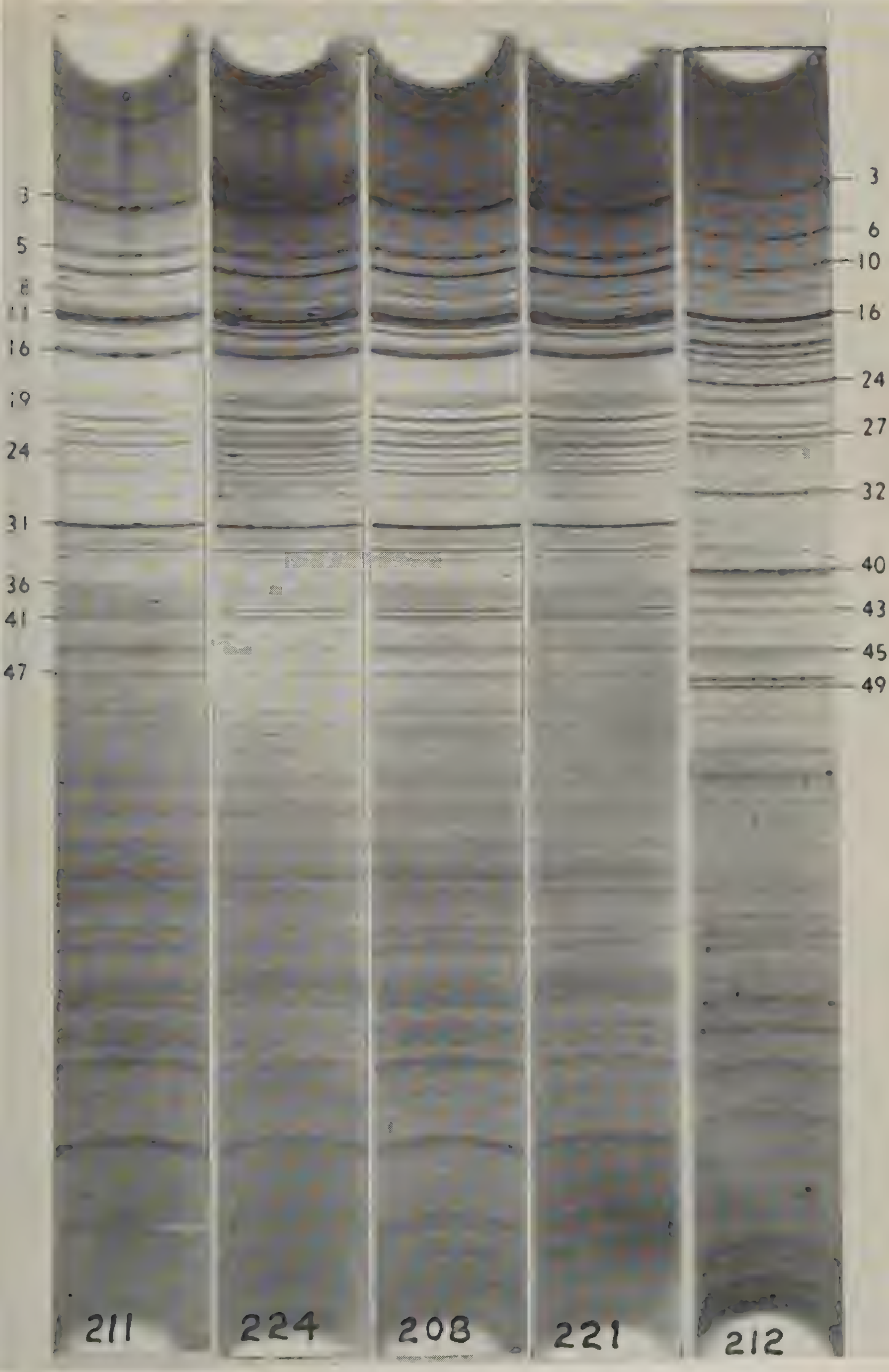

FIG. 1. *X*-ray powder films of (left to right) Finnish morinite, Saxon ježekite, Black Hills morinite, French morinite and Austrian [illegible]. All taken with Fe/Mn radiation in a 114 mm. diameter Straumanis-type (Philips) camera. Approximately natural size. See Table 2 for measured data and numbering of lines.

Table 2. Powder Film Data

Line No.	Ježekite (Saxony)			Morinite (Black Hills)		Epidote (Untersulzbachtal)		
	Int.	*d*	Indices	Int.	*d*	Int.	*d*	Indices
1	6	9.115#	100	6	9.11	1−	8.00	$\bar{1}01$, 100
2			$\bar{1}01$	1−	5.22#	½	7.01	Not indexable
3	8	4.698#	011, $\bar{1}11$	7	4.70	4	5.01	$\bar{1}02$
4			111	1	3.83	½	4.64	110
5	7	3.742#	$\bar{2}11$	6	3.73	½	4.42#	$\bar{2}01$,[1]
6	9	3.472	220	8	3.47	4	4.00	$\bar{2}02$, 200
7			130	1	3.32	½	3.78	111,[2]
8	4	3.212#	$\bar{2}21$	2	3.21	1	3.76#	$\bar{1}12$
9	2	3.069	201	2	3.08	1	3.59	(beta for line 12)
10	2	3.006	$\bar{3}01$	2	3.00	3	3.52	$21\bar{1}$
11	10	2.945	031, $\bar{1}31$	10	2.94	2−	3.40	102, $\bar{1}03$
12	3	2.888	$\bar{3}11$	4	2.88	2	3.24	201, 210
13	3	2.805	230	3	2.81	½	3.18	$\bar{2}03$[3]
14			040	2−	2.69	½	3.06	003
15			$\bar{2}31$	1	2.66	*	2.97	$\bar{3}02$, ($\bar{3}01$)
16	8	2.631#	$\bar{1}12$, 320, 002	7	2.63	10	2.92	$\bar{1}13$, (112)
17	1	2.553	012	½	2.56	2	2.815	020, 211
18	2	2.372#	301, 102, $\bar{1}41$	1+	2.37	½	2.78	$\bar{2}13$
19	3	2.309#	$\bar{3}02$, 311	2−	2.31	5	2.69	013, 021, 300
20	6	2.230	141, 410, $\bar{2}41$	4	2.23	1	2.66	120, ($\bar{3}03$, $\bar{1}21$)
21	3	2.163#	321, 122	3	2.16	5	2.62	$31\bar{2}$, $31\bar{1}$
22			$\bar{4}21$	¾	2.13	2	2.53	202, (103)
23	4	2.098	$\bar{2}32$, 420	3	2.10	1	2.46	$\bar{1}22$, (121)
24	3	2.056	202	2	2.055	7	2.40	$\bar{3}13$, 022, $22\bar{1}$
25	3	2.017	212, 241	2−	2.015	3	2.30	$\bar{3}04$, $\bar{2}14$, $\bar{1}14$ $\bar{2}22$, 113
26	4	1.979	$\bar{1}51$	2	1.98	2	2.17	$\bar{4}01$, $\bar{1}23$ 122, ($\bar{4}03$)
27	1	1.920#	222, 430	1	1.925	3	2.13	221, $\bar{2}23$, (014)
28	1	1.886#	$\bar{5}01$, $\bar{4}22$, $\bar{2}42$	1+	1.89	2−	2.07	023
29	1	1.830#	500	1−	1.83	½	2.05	203
30			421, 510	½	1.80	½	2.02	400, 104, $\bar{2}05$

TABLE 2—(*continued*)

Line No.	Ježekite (Saxony)			Morinite (Black Hills)		Epidote (Untersulzbachtal)		
	Int.	*d*	Indices	Int.	*d*	Int.	*d*	Indices
31	9	1.786	060, $\bar{1}$13, 232	8	1.783	$\frac{1}{2}$	1.93	213, $\bar{2}$15
32				1	1.75#	4	1.88#	$\bar{2}$24, 123, $\bar{1}$24 222, $\bar{1}$15, 114
33				1−	1.73	$\frac{1}{2}$	1.78	$\bar{5}$02
34	3	1.712		3	1.71	$\frac{1}{2}$	1.75	$\bar{4}$22?
35	1	1.689		1+	1.687	$\frac{1}{2}$	1.73	$\bar{2}$31, 032
36				1	1.615	1	1.71	204, $\bar{2}$06, $\bar{4}$15
37				1−	1.60	1	1.69	
38				1	1.59	$\frac{1}{2}$	1.673	
39	1	1.575		1	1.572	4	1.641	$\bar{5}$11
40	2	1.559		2	1.56	2	1.63	
41	3	1.542#		1+	1.546	1	1.59	
42				1	1.532	2−	1.58	
43	1	1.507#		$\frac{1}{2}$	1.51	2−	1.548	
44	1	1.492#		$\frac{1}{2}$	1.492	1	1.533	
45	2	1.474#		2	1.476	2	1.461	224, $\bar{6}$04
46				2	1.468	$\frac{1}{2}$	1.45	
47	1	1.428#		2−	1.428	1	1.44	
48				$\frac{1}{2}$	1.386#	3	1.412	040
49						3	1.395	

# Diffuse line.

* Present with intensity 3 on some synthetic epidote films; not given by the Untersulzbachtal epidote.

[1] Probably a beta reflection for line 6.

[2] Probably a beta reflection for line 11.

[3] Probably a beta reflection for line 16.

Indices given in parentheses make only minor intensity contributions.

NOTE. The ježekite film was measured accurately by Leon Atlas; the other two measurements were made by Fisher using a Nies scale. The ježekite and French morinite samples were supplied by F. Čech of the Mineralogical Institute of Charles University (Prague) through the kindness of J. Kutina. The Finnish sample was supplied by A. Volborth. Indices were computed graphically by Fisher using the Peacock-Bloss technique (*Am. Mineral.*, **37**, 1952, 588–599). From a number of films the six stronger lines of morinite-ježekite (with intensities) were found to be: 2.94/10; 3.47/9; 2.63/8; 1.79/7+; 4.07/7−; and 3.74/6.

former agree in general with those of Murdoch for ježekite from Brazil, but the spacing for his first line should probably be 9.11 rather than 9.61. Volborth (p. 74) states that a sample of French morinite collected by Lacroix gave him an *x*-ray powder pattern identical with that he obtained from the Finnish morinite.

Precession and Weissenberg films were made from a single prismatic crystal of Black Hills morinite. The unit cell dimensions are $a_0 = 9.456$ Å, $b_0 = 10.690$, $c_0 = 5.445$. The space group is $P2_1$ or $P2_1/m$, almost certainly the latter when account is taken of the morphology. The *b*-axis is a screw, since the only systematic extinctions are those for $(0k0)$ where k is odd. β was found to be $105°27\frac{1}{2}'$. This leads to an axial ratio of 0.8846:1:0.5094. This may be compared to Slavik's determination for ježekite of 0.8959:1:1.0241 with β of $105°31\frac{1}{2}'$. The agreement is satisfactorily close if Slavik's *c*-value is halved. Transformation formula, Slavik to Fisher is thus $100/010/00\frac{1}{2}$.

The Black Hills crystal (0.2805 mm. thick along the *b*-axis, and 0.2020 mm. thick along the a^*-axis and about 3 mm. along *c*) has *b*(010), *a*(100), *m*(110), *n*(120), *l*(210), *f*(011), *r*($\bar{1}$01), *u*($\bar{2}$01) and *p*($\bar{2}$11). Forms *e*(021), *t*(102), and *s*(101) found by Slavik on the Greifenstein ježekite are not present on the Black Hills crystal. Note that all these indices are given in terms of Fisher's axial ratio, but Slavik's letters are retained. The Black Hills crystal has only one "line" face ($\bar{1}$20) and ($\bar{2}$10) showing for *n* and *l*, and only ($\bar{2}\bar{1}$1) of the *p*-form is present on the crystal, but it is the largest face found; the crystal is terminated only at one end.

The Black Hills crystal is (−) with $\gamma \leadsto b$ and $\beta\wedge c$ of $-60\frac{1}{2}°$ (that is, the β direction lies in obtuse angle β). This was determined on the same crystal on the same goniometer head (no remounting) used for the *x*-ray work, by placing it on the universal microscope-goniometer (Fisher, 1952). Using the technique described for alluaudite (Fisher, 1955) the birefrigence for Na light was found to be $\gamma-\alpha = 0.01400$ and $\beta-\alpha = 0.01234$. This leaves by difference that $\gamma-\beta = 0.00166$. Using these values and assuming $\alpha = 1.55100$ (approximate measurement by Runner) 2V is calculated at 39°42′. For the Greifenstein ježekite Slavik gives extinction on (010) in obtuse angle β as $\alpha\wedge c = 29°$ and $b=\beta$; Larsen and Berman state $\alpha\wedge a = 29°$, $b=\beta$. For the French morinite Lacroix notes that the acute bisectrix (−) makes an angle of about 30° in obtuse β, and that the optic plane is (010); Larsen and Berman give $b=\beta$, extinction at 30° in obtuse angle β, and 2V = 38° ±. These results are very different from those found for the Black Hills morinite.[1] For the Viitaniemi morinite Volborth has $b? = \gamma$ with $(001)? \wedge \alpha = 44°$, but he is not certain as regards his morphology. Fisher's findings show $(001) \wedge \alpha = 45°$; thus check Volborth's results almost perfectly, confirming his choice of indices.

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[1] It is difficult to understand how both Lacroix and Slavik found the optic plane to be (010). That they put direction α in obtuse angle β (rather than in acute angle β) at an angle of 30° to the *c*-axis is perhaps explicable since $\rho_{(001)} = 15°27\frac{1}{2}'$ and $\rho_{(\bar{1}01)} = 17°47'$. In short an alternative orientation for morinite is to reverse the direction of the (+) *a*-axis making

TABLE 3. ANALYSES OF MORINITE AND JEŽEKITE

	I	II	III	IV	V	VI	VII	VIII
CaO	24.11	23.92[1]	18.16	19.05	17.27	11.63	12.84	13.50
Na_2O	6.66	7.16[2]	3.35	5.13	6.36	25.72	25.74	27.07
Al_2O_3	21.92	22.20	22.01	17.56	20.93	21.15	20.84	21.92
P_2O_5	30.52	30.16[3]	30.65	33.05	29.14	29.45	28.81	30.30
F	12.26	11.49	14.36	13.02	13.65	7.88	7.75	8.15
H_2O	9.68	9.90	17.51	17.66	18.40	7.48	7.31	7.69
Total	105.15	104.83[4]	106.04	105.47	105.75	103.31	103.29	108.63
−O for F	5.16	4.84	6.04	5.48	5.75	3.32	3.26	3.46
Total	99.99	99.99	100.00	99.99	100.00	99.99	100.03	105.17
D	2.911	2.957	2.90	2.94	3.06	3.02	2.94	2.94

Explanation of columns

I. Composition calculated for formula $Ca_4Na_2Al_4F_6OH_4\ (PO_4)\cdot 3H_2O$.

II. Finnish morinite (Volborth, p. 77). Footnotes:

[1] Including .09 SrO and 2.47 MnO; this is $\frac{1}{3}$ ion of Mn per unit cell.

[2] Including .14 Li_2O and .18K_2O.

[3] Including .28 BeO and .49 SiO_2.

[4] This omits .17 $H_2O(-)$ and .17 insoluble residue.

III. Composition calculated for formula $Ca_3NaAl_4F_7(PO_4)_4\cdot 9H_2O$.

IV. French morinite (Carnot & Lacroix, 1908) summed to 100% (after eliminating 1.50 SiO_2 and 0.20 H_2O-).

V. Composition calculated for formula $Ca_3Na_2Al_4F_7OH(PO_4)_4\cdot 9H_2O$.

VI. Composition calculated for formula $Ca_2Na_8Al_4F_4(OH_8)(PO_4)_4$.

VII. Composition in Column VIII made to sum to 100%.

VIII. Saxon Ježekite (Skarnitzl, in Slavik, 1914) with 1.85% Li_2O included with Na_2O. Skarnitzl lists 18.71 Na, 0.86 Li, 7.26 OH, and trace of Fe_2O_3. He sums to 100.70. In the above, his values for Na, Li, & OH are converted to oxides.

The Black Hills specimen is suitable material to furnish a good chemical analysis, but at the moment no chemist is available. If we take Volborth's analysis (see col. II of Table 3) of the Finnish morinite and assume the unit cell volume is 530.5 Å³ and the specific gravity is 2.96, the unit cell contents (allocating the minor elements as follows: Li and K with Na; Mn and Sr with Ca; Be and Si with P) are calculated to be:

$$Ca_{3.91}Na_{2.19}Al_{4.08}F_{5.66}P_{4.06}O_{18.24}\cdot 5.15H_2O.$$

$\beta = 107°47'$ with direction α lying in obtuse angle β. Volborth has the cleavage as (010)? and (001)?, whereas Lacroix and Slavik both make it (100); Slavik also lists (001) as an imperfect cleavage.

This can be recalculated to:

$$Ca_{3.91}Na_{2.19}Al_{4.08}\ [F_{5.66}\ OH_{4.09}]\ P_{4.06}\ O_{16.24}\ \cdot 3.15H_2O$$

which can be written:

$$(Ca,\ Na)_{6.10}Al_{4.08}\ [F,\ OH]_{9.66}\ P_{4.06}O_{16.24}\ \cdot 3.15H_2O$$

Volborth notes that the F-content should be about 1.3% higher than shown in the analysis; thus the ideal unit cell contents would seem to be very close to:

$$Ca_4Na_2\ Al_4(F,\ OH)_{10}\ P_4O_{16}\cdot\ 3H_2O.$$

Actually all of the "water" in this analysis came off at +105°. Thus writing the analysis with $3H_2O$ and 4 OH is really a purely artificial technique which permits one to balance the analysis in convenient fashion. Thermogravimetric and perhaps infra-red studies are needed to tell more about the nature of the "water" as it actually occurs in the crystal.

At first glance it appears as if morinite might bear some crystallochemical relationship to epidote, since unit cell dimensions and chemical composition seen to have resemblances; thus:

	S.G	*a*	*b*	*c*	*β*	*Z*	*V*	*D*
Epidote[1]	$P2_1/m$	8.905 Å	5.636	10.145	115°23′	2	460	3.47
Morinite	$P2_1/m$	9.456 Å	2(5.345)	½(10.890)	105°28′		530	2.96

Epidote	Ca_2	$(Al,\ Fe)_3$	(OH)	Si_3O_{12}	
Morinite[2]	$(Ca,\ Na)_{4-8}$	Al_3	$(F,\ OH,\ O)_{5-9}$	$P_3O_{12}\cdot 0\text{–}2\ H_2O$	

This apparent similarity is enhanced when one plots (on a projection normal to the *b*-axis) the 0-level planes of the lattices of these two minerals, providing the *a*-axis of epidote is made to coincide with the $\bar{c}$-axis of morinite. In this case it is clear that there are a number of lattice points substantially in common; such common points form a pseudohexagonal network. Since the (100) spacing for morinite is only 0.57% less than the (001) spacing for epidote[3] (a^* is .1097 for morinite and c^* is .1091 for epidote), if the 0-levels (normal to the *b*-axis) of the reciprocal lattices for the two are plotted, not only do the $(h00)^*$ nodes of morinite practically coincide with the $(00l)^*$ nodes of epidote, but the nodes of the morinite third row (parallel a^*) nearly coincide with those of the epidote fifth row (parallel c^*); the reciprocal spacing for this row in morinite is 0.551 and in epidote it is only about 0.011 greater.

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[1] New determination on an Untersulzbachtal crystal by Fisher; values ±.003Å. This crystal is (−) with $2V=73°00'$ and $\alpha\wedge[c]=-5°17'$ (Na light).

[2] Approximate average of the two morinite and one jezekite formulae given in Volborth.

[3] This does not show up well on the powder films (see Fig. 1), since the only moderately strong "front pinacoid" line of morinite is (100) [though (500) makes an important contribution to a weak line], while the only "basal pinacoid" line for epidote is the weak (003). The powder films of the two minerals are on the whole rather dissimilar (see Fig. 1); though each has its strongest line at 2.93±.01, this seems not to be due to any common structural condition.

However, when the formula for epidote is written to fit the structure determined by Belov and Rumanova or by Ito *et al:*

Epidote—Ca_2 $[Al_2(Al, Fe)]$ Si_2O_7 $(OH\ O)$ SiO_4,

since Z = 2, it is seen that there are six silicate tetrahedra (4 double, 2 single) in the unit cell, as opposed to only four phosphate tetrahedra in the morinite unit cell. The data as regards the unit cell contents (omitting the $3H_2O$ of morinite) are summarized in Table 4.

TABLE 4. UNIT CELL CONTENTS

(Omitting $3H_2O$ of morinite)

Cation	Morinite	Epidote	Anion	Morinite	Epidote
Ca	4	4			
Na	2	—	F	6	—
Al	4	4	OH	4	2
Fe'''	—	2	O	16	24
P	4	—			
Si	—	6			
Total	14	16		26	26
Unit cell volume	530	460	Vol. per anion	20.4	17.7
$\sum$ valencies	42	50	D	2.91	3.47

The greater density (D) of the epidote may be attributed largely to the presence in the unit cell of 2Fe (rather than 2Na), of two more Si (than P); and of only 2% H_2O. The difference in unit cell volume is of little significance in this connection, since the extra volume of the morinite cell is necessary to pack in the larger Na (than the smaller Fe), and especially to hold the $3H_2O$. If the latter be assumed to add the volume of 3 anions to the unit cell, the volume per anion is reduced from 20.4 (see Table 4) to 18.3, a figure not significantly different from the 17.7 of epidote. But this comparison is not very rigorous, since the morinite unit cell contains two large cations (sodium) absent in epidote.

The unit cell contents clearly indicate that morinite is a nesophosphate (unless some of its aluminum is in 4-coordination), whereas epidote was found to be a combination neso- and sorosilicate. Thus the two structures would seem to be quite different, even though geometrically and chemically they have much in common. The concept that morinite has sort of a "stuffed" epidote structure seems very doubtful. This is borne out by the differences in the powder diffraction patterns; see Fig. 1.

Analyses of the French morinite (IV) and Saxon ježekite (VII) also appear in Table 3. The formula for the latter as given in Pabef (II, 785) seems unsatisfactory because of the lack of agreement between analyzed and theoretical OH. The actual unit cell contents of the French morinite are computed to be:

$$Ca_{3.19}Na_{1.55}Al_{3.24}F_{6.44}P_{4.37}O_{16.26}\cdot 9.21H_2O.$$

This may be idealized as:

$$Ca_3NaAl_4F_7(PO_4)_4\cdot 9H_2O.$$

or as:

$$Ca_3Na_2Al_4F_7OH(PO_4)_4\cdot 9H_2O.$$

The actual unit cell contents of the Saxon ježekite are computed to be:

$$Ca_{2.15}(Na, Li)_{8.37}Al_{3.84}F_{3.83}OH_{7.62}P_{3.81}O_{15.895}.$$

This may be idealized as:

$$Ca_2Na_8Al_4F_4OH_8(PO_4)_4.$$

The analyses on which these formulae are based were made long ago. It was with considerable difficulty that enough material was obtained. It is not surprising that they show disagreements. The presence of 1.1 ion of Li in the ježekite unit cell seems very doubtful; more probably there was some amblygonite contamination. In both of these analyses an attempt was made to balance fluorine (or F+OH) against calcium (France) or the alkalies (Saxony) as was customary in those days. In the former case there was insufficient calcium, in the latter excess alkalies. If the ježekite analysis is recast from the partly-elementary form as given (see Pabef) into the oxide form (col. VIII of Table 3) it is seen that it sums to 105%, indicating serious errors somewhere.

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NOTES AND NEWS

THE COMPOSITION AND PHYSICAL PROPERTIES OF GARNET

Horace Winchell, *Geology Department, Yale University*

Diagrams relating physical properties to chemical composition are familiar to all mineralogists. An exhaustive list of citations to such diagrams would be impossible here, but would include such books as Troeger (1956) and Winchell (1951), and a great many shorter articles such as those of Sriramadas (1957), and Kennedy (1947). With only a few exceptions (as Ford, 1915), such charts show the physical properties such as one or more refractive indices, lattice constants, melting, inversion, and decomposition temperatures, specific gravity, etc., by means of contour lines drawn over diagrams in which the main coordinates are determined by chemical composition. Yet the commonest use of these charts is probably for determining composition from the physical measurements. The usual arrangement is clearly best if there are more physical parameters than chemical ones—but that condition is not necessarily satisfied, especially if physical parameters are limited to those that can be conveniently measured. An important example in which exchange of the dependent and the independent variables may be useful is the garnet system, where at least five chemical components should be determined, but the conveniently measured physical properties are only refractive index n, lattice constant, a, and specific gravity G.

Garnet Diagram

Since the early work of Ford (1915) there have been several systematic efforts to estimate or measure the refractive index, n, specific gravity G, and lattice constant a, of the five principal components of the garnet system, grossularite (*abbr.* gro), andradite (and), almandite (alm), spessartite (sp), and pyrope (pyr); the latest seem to be those of Skinner (1956), on synthetic materials, and of Fleischer (1937) on analyzed natural materials, from which properties of the components were derived by extrapolation. Kennedy (1947) collected eight triangular diagrams showing all but two of the three-component subsystems possible in the five-component garnet system, with contour lines showing refractive indices and densities of the three-component compounds. Sriramadas (1957) used similar triangular diagrams but showed contours of indices and lattice constants, based on the more recent data of Skinner (1956). To utilize all combinations of the conveniently measurable data a, n, G, yet another set of similar diagrams would be needed, with contour lines of G and a. Perhaps it would be better to add the G-contours to the diagrams of Sriramadas.

The implied assumption in these diagrams is that the physical properties represented on each triangle are additive functions of the molecular proportions of the compounds A, B, and C, at the corners; thus the refractive index of a sample would be

$$n = n_A x_A + n_B x_B + n_C x_C \qquad (1)$$

throughout the subsystem A-B-C, where n_A, etc., are the indices of the pure components, and x_A, etc., are their respective molecular proportions in the sample. This equation can be extended to include any number of additional components, as D, E, F, etc., but graphical presentation becomes increasingly difficult as more components are considered (Mertie, 1948). Fleischer (1937) proved empirically that this type of relationship is at least a very good approximation for natural garnets, although Zen (1956) shows that the relation for a is at best only a first approximation to the truth if volume effects are additive.

Rather than trying to show the dependence of three physical properties on the five chemical components in the garnet system, it would seem reasonable to treat two of the properties as independent variables and show the several chemical compositions, and the third physical property, as functions of the two chosen properties. We concur with Sriramadas that the index and the lattice constant are probably the best-measured physical properties; hence we use these as ordinate and abscissa, respectively, in Figs. 1 and 2, and locate the points corresponding to each of the end-member components as summarized by Skinner (1956). To avoid excessive confusion of lines on the diagram, only four components (pyr, alm, gro, and and) are shown in Fig. 1, with straight lines connecting them in pairs to represent in conventional manner the chemical variations in the corresponding binary series. These straight lines outline four triangles, the faces of a skew tetrahedron, and contour lines on these triangular faces show the variations of the specific gravity G.

Fig. 2 shows the same four components, and a fifth (spessartite), with contour lines plotted on the six triangular fields that have spessartite as one corner. Using inks of several colors, it is possible to show all ten triangular fields on the same diagram without undue confusion, but here the data are better separated as in Figs. 1 and 2. The point representing uvarovite (uv) is shown, but the effect of that component on garnets in general is not indicated. Its properties $a = 11.955$, $n = 1.861$, $G = 3.895$, were obtained by extrapolation from the data of Knorring (1951), with minor adjustments to maintain general self-consistency of all data used in Figs. 1 and 2. The form of these diagrams is analogous to that published by Ford (1915, Fig. 9), who plotted n and G as abscissa and ordinate, without drawing the composition triangles. Winchell (1951 and earlier editions) used the same basis to construct a diagram showing the

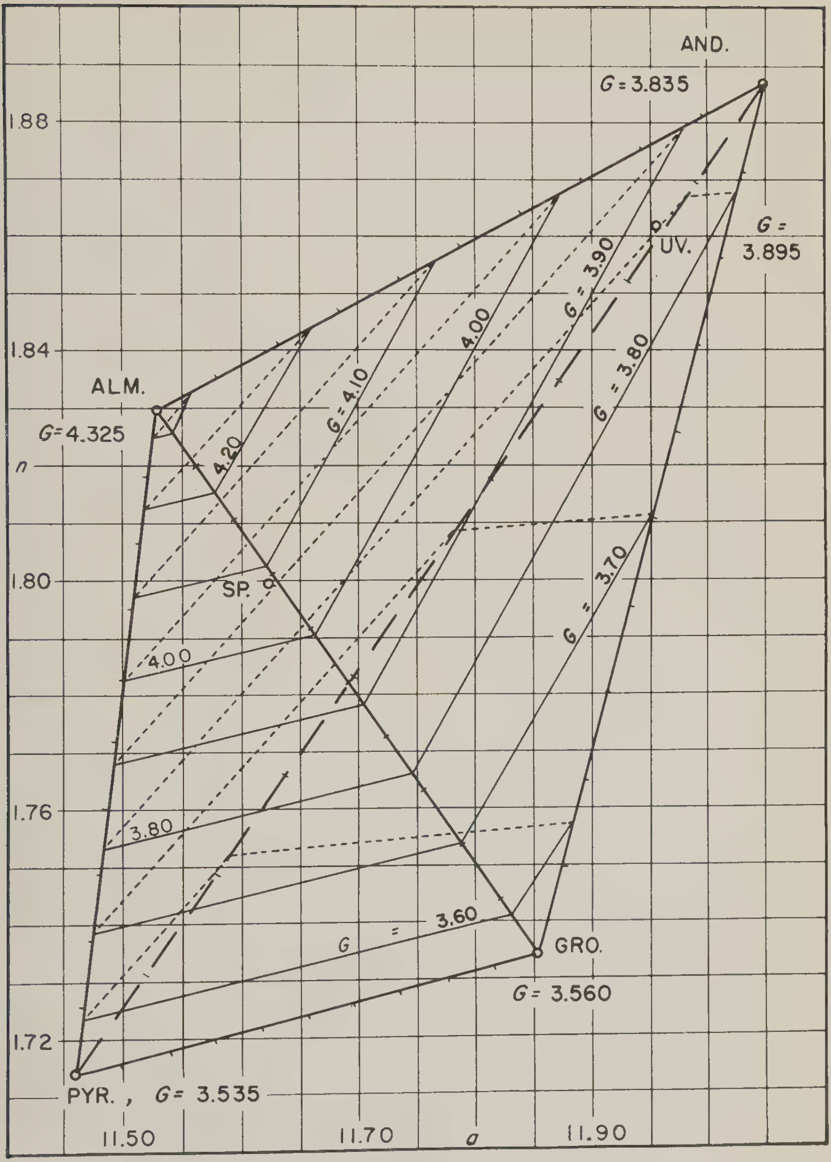

Fig. 1

estimated properties of the pure components or "end-members," and drew sufficient networks of lines between them to enable the user to interpolate conveniently in the systems that are geologically most significant. In the accompanying Figs. 1 and 2 this scheme is carried out more fully,

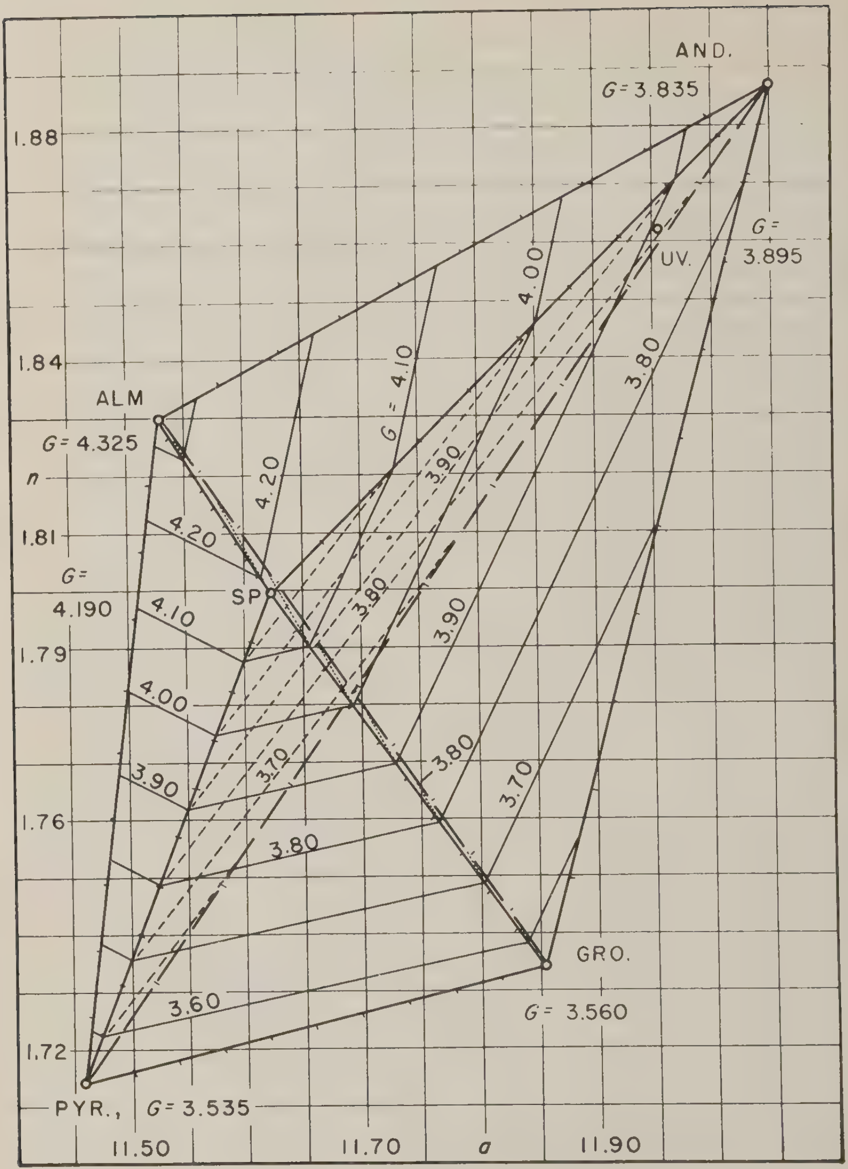

FIG. 2

with the best data now available. Short ticks at equal intervals along the boundaries of the several triangles show 10-percent increments of composition for each binary series; they can be connected by light lines to facilitate reading from the diagram the composition corresponding to any point within one of the triangles. In many cases the contoured specific gravity data resolve ambiguities due to overlap of the three-component composition fields, and in some cases the contours may even permit estimates to be made on the basis of the four-component composition regions enclosed by one of the tetrahedrons.

Thus, for example, if a garnet of unknown composition has $a=11.550$, $n=1.770$, and $G=3.880$, its composition may be estimated by reference in Fig. 1 to the triangle pyr-alm-gro as mostly $pyr_{55}alm_{45}$ (found by drawing a line through the apex "gro" and the given point so as to cut the "pyr-alm" base of the triangle at $pyr_{55}alm_{45}$), modified by about 17% of gro, i.e., $pyr_{46}alm_{37}gro_{17}$; the contour lines show that such a garnet would have $G=3.894$. Similarly in Fig. 1, the composition could also be $(pyr_{66}alm_{34})+13\%$ and, or $pyr_{57}alm_{30}and_{13}$, for which $G=3.808$; Fig. 2 shows that the same point may also represent a garnet with composition $pyr_{38}alm_{9}sp_{53}$ and $G=3.950$. The measured value, $G=3.880$, lies 0.84 of the way from $pyr_{57}alm_{30}and_{13}$ to $pyr_{46}alm_{37}gro_{17}$, and the composition may therefore be estimated as $pyr_{48}alm_{36}gro_{14}and_{2}$, found by adding .84 $(pyr_{46}alm_{37}gro_{17})$ and .16 $(pyr_{57}alm_{30}and_{13})$. Alternatively, we find by similar reasoning the composition $pyr_{47}alm_{20}sp_{27}and_{6}$; in fact, there is a 5-component series between these two 4-component compositions, in every part of which the required a, n, and G would be the same. A geological mineralogist would use such other data as a qualitative test for Mn, and/or mineral associations in the rock, to fix this specimen at or very near the correct composition along such a series. It is hardly necessary to emphasize again the assumptions on which such use of Figs. 1 and 2 are based—(a) the accuracy of the data used in their construction, (b) the adequacy of "Vegard's law" for the rather small ranges of values of physical properties involved, and (c) that for the specimen at hand, other components are insignificant compared to the five used in the calculation. With these limitations clearly in mind,—limitations that apply equally to other types of charts , the two diagrams here presented may be used conveniently in place of the ten triangular diagrams representing faces of Mertie's (1948) 4-dimensional hypertetrahedron, eight of which were given by Kennedy (1947), and by Sriramadas (1957). Levin (1950) has described an algebraic solution that he carries out on a desk-type electric computer in about 20 minutes per determination, using measured variables a, n, G, and the weight-percentage of MnO or of FeO.

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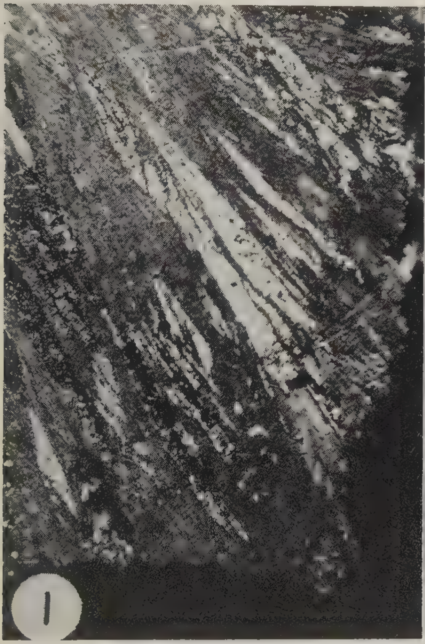
DAHLLITE PSEUDOMORPHS AFTER PYRITE CONCRETIONS FROM BIG HORN BASIN, WYOMING

Richard S. Mitchell and W. Cullen Sherwood,
University of Virginia, Charlottesville, Virginia

The occurrence of spherulitic phosphate concretions in the basal part of the Thermopolis formation (Upper Cretaceous) in the Big Horn Basin, Wyoming has been known for over fifty years. Fisher (1906) described these concretions as consisting mainly of "phosphate of lime" and having the structure of marcasite, the mineral he believed the phosphate had replaced. McConnell (1935) published a thorough petrographic description of these concretions. In his work he determined they are composed primarily of dahllite, the carbonate-hydroxyapatite. The suggestion was made that the forms might represent replacement, but he was unable to find relicts of a replaced material. The purpose of this note is to present evidence that indicates these masses are actually pseudomorphs of dahllite after pyrite. The specimens used in this study were collected by the senior writer in the summer of 1955 near Rainbow Canyon on the eastern edge of the Big Horn Basin.

The concretions are spherical in shape, frequently have a rough external surface, and average slightly over one inch in diameter. In cross section the specimens always exhibit a radial structure and show a rather consistent arrangement of their mineral constituents. At the center of all the concretions studied is an irregular mass of iron oxide which is often stellate in shape. This oxide was determined to be primarily goethite in all but one instance where hematite was found to be predominant. From the iron oxide center gray-brown dahllite extends to the surface of the spheres and constitutes the major portion of the spherulites. The concretions frequently contain an external crust of earthy light-gray dahllite. Kaolinite is present in small cavities which are parallel to the general radiating structure. Pyrite, while occurring in all the specimens studied in detail, was present only in one specimen in sufficient quantities so as to be visible in the hand specimen. The pyrite in this specimen was in a radial form (Fig. 1).

Determinations of all mineral constituents of the concretions were verified by the powder x-ray diffraction method. Four patterns each of the dahllite crust, interior dahllite, interstitial clay, and iron oxide center were obtained from four different specimens. Interplaner spacings for the crusty and the interior phosphate indicate they are identical. However, a finer grain size in the crusty material is indicated by slightly more diffuse x-ray lines. A comparison of these interplaner spacings with those obtained by McConnell (1938) for dahllite reveals identical materials. Measurements of the clay patterns clearly show this material belongs in the kaolinite group, but a more precise categorization proved inconclu-



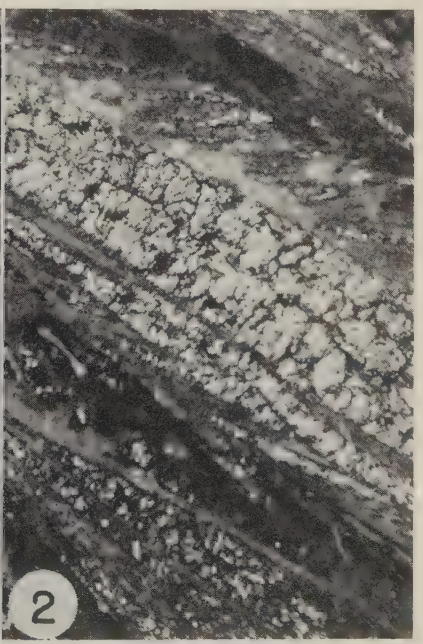


Fig. 1 (left). Photomicrograph of a polished cross section of spherulite showing the radial arrangement of pyrite (white) and dahllite (gray). Obliquely reflected light. ×22.

Fig. 2 (right). Photomicrograph of a thin section showing the replacement of pyrite (white) by dahllite (gray). Notice isolated blebs of pyrite. Crossed nicols plus obliquely reflected light. ×72.

sive. Three of the iron oxide films revealed impure goethite, while the fourth showed hematite. A good pyrite pattern was obtained from one specimen.

Good evidence for the replacement origin of the phosphate was found in a study of thin sections of the specimen mentioned above which contains much pyrite visible to the unaided eye. These sections show many small veins of dahllite penetrating the radial pyrite. In some places the pyrite has been replaced to such an extent that it remains only as small blebs and elongate islands which are aligned more or less parallel to the radial structure of the spherulites. Some of these features are shown in Fig. 2. An examination of thin sections of several other specimens, with no pyrite visible to the naked eye, showed that relict pyrite is common in the form of these blebs and oriented elongate islands. The presence of iron oxide rims around some of these unreplaced pyrite areas suggests that oxidation was subsequent to phosphatization. Perhaps the larger areas of goethite and hematite present in the center of most specimens represent oxidized pyrite. Small specks of pyrite are frequently visible in these larger oxide areas.

The translucent brown goethite shows a fine fibrous structure in thin sections. These fibers show parallel extinction. Textural evidence indicates that part of the star-like goethite may represent crack-fillings in the concretions. Stellate cavities are known to the writers to occur in pyrite concretions from some localities. Opaque and red hematite, frequently in the form of hair-like veins and irregular blebs, is associated with the goethite in some specimens.

Thin sections show that dahllite varies in size from powdery masses to microscopic hexagonal prisms. The specimen containing much pyrite mentioned above consists of powdery dahllite. The clearly visible radial structure in this one is completely isotropic and is probably reminiscent of the former pyrite structure. Thin sections show that the radial appearance of the concretions is not due to a parallel alinement of dahllite fibers In fact most specimens showed dahllite microlites both parallel and transverse to the pyrite fiber directions. The present radial appearance is most likely a result of controlled replacement by the former pyrite fibers. Small euhedral crystals of dahllite, exhibiting prisms and pinacoids, are commonly found in cavities in the specimens. All crystals and fibers proved to be length fast when tested with the gypsum test plate. Similar forms and characteristics of dahllite were previously described by McConnell (1935). Microscopic study also showed the presence of cavity fillings of kaolinite and quartz in parallel position to the original pyrite fibers. The general relationships indicate these were deposited in openings subsequent to the formation of dahllite. Other detrital-like quartz grains, having no relationship to the spherulitic structure, were occasionally observed in the sections.

A striking identity was noted between the structure of these concretions and an unaltered pyrite concretion from a different locality which was sectioned for comparison. The writers feel this similarity, along with the evidence presented above concerning replacement, indicates that these dahllite spherulites are pseudomorphs after pyrite.

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THE MELTING OF CALCITE IN THE PRESENCE OF WATER AND CARBON DIOXIDE

M. S. PATERSON, *Department of Geophysics, Australian National University, Canberra, Australia*

In the course of attempts to recrystallize calcite, it was found that the calcite could be melted at temperatures above about 900° C. in an atmosphere of water and carbon dioxide at a total pressure of 50 bars. The experiments were done in the following way. The specimen, of about 0.1 gm. weight, was wrapped in platinum foil and put in a pressure vessel, supplied by G. C. Kennedy, of approximately 1 cc. volume. A few drops of water were introduced and the pressure line was connected to a reservoir of carbon dioxide at 50 bars pressure. The pressure vessel was then put in a muffle furnace at the desired temperature. This produced an atmosphere in which the partial pressures of carbon dioxide and water totalled 50 bars but the proportions were not known. The same total pressure was maintained during the cooling of the pressure vessel.

The melting is best demonstrated with a cleavage rhomb of calcite. If this is heated under the above conditions at about 1000° C. for an hour, its original shape is lost and the material takes the shape of the enveloping platinum as if it were wetting the platinum (Fig. 1A). After cooling, a thin section of the specimen shows it to be polycrystalline, with a marked dendritic texture (Fig. 1B) which suggests that it has crystallized from a melt. An x-ray diffraction pattern shows no trace of CaO. Further evi-

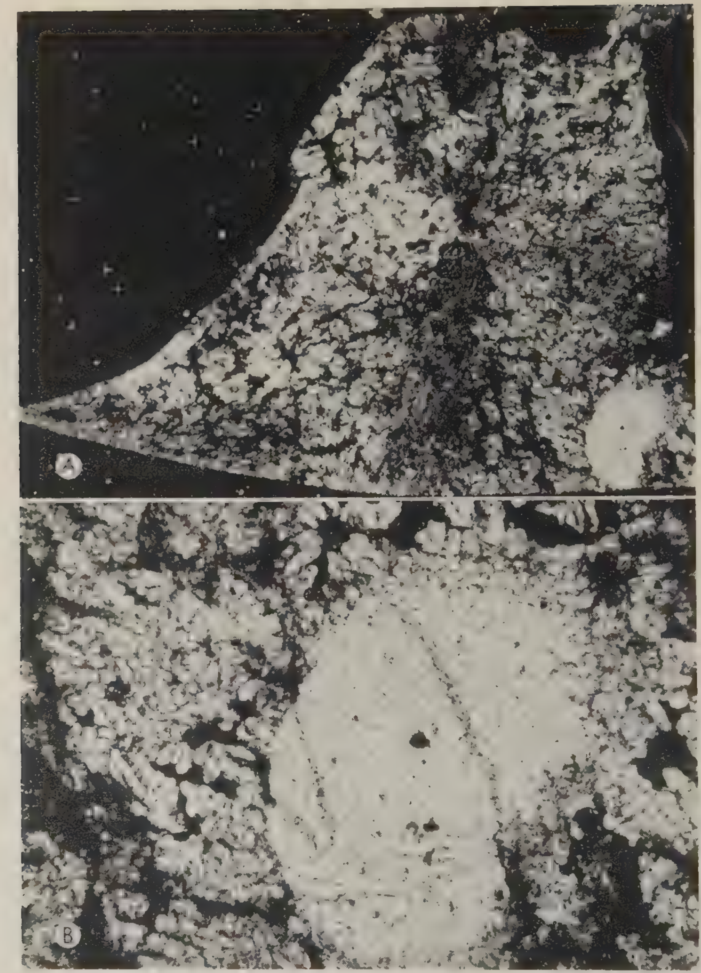

FIG. 1. Thin section of calcite after melting in the presence of CO_2 and water at 1000° C.
A. Complete specimen. ×12.
B. Bottom right corner of A, showing remnant of initial crystal surrounded by dendritic crystals. ×54.

dence that the calcite has been melted is obtained if the pressure is released while the pressure vessel is hot; the resulting specimen has a vesicular texture, suggesting the escape of bubbles of gas from a viscous liquid.

Melting of a thin surface layer of the calcite was apparent at temperatures down to about 900° C. under the same conditions, but very little effect was observed below 900° C. After heating at 930° C. well-formed dendrites of lengths up to 1/10 mm. were seen in cavities in the layer of material that had apparently melted (Fig. 2).

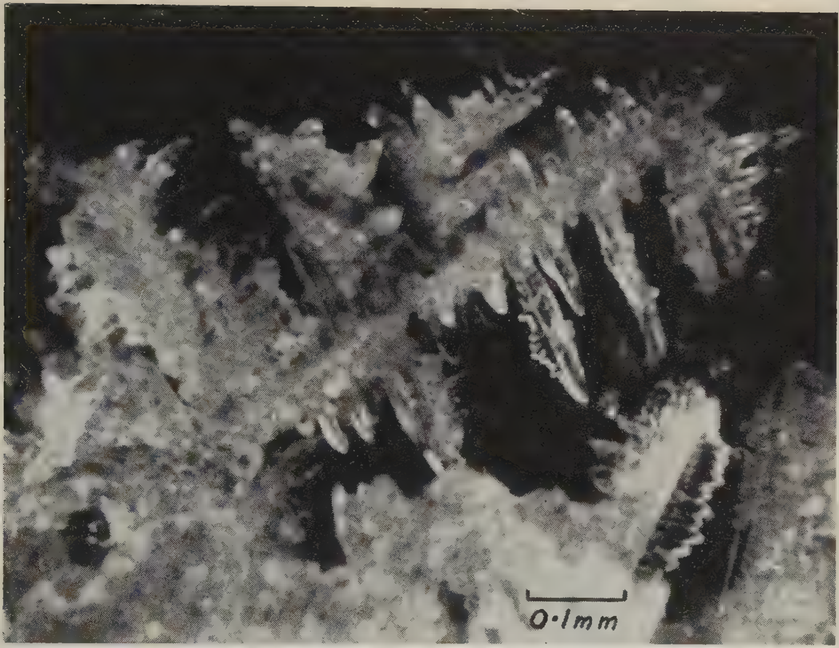

FIG. 2. Dendrites of calcite in cavity in melted and recrystallized grain. Formed at 930° C.

Since the experiments were not done in a closed system, the conditions for melting the calcite are not exactly known; it is even likely that conditions in the pressure vessel changed during the course of heating. Therefore, the principal conclusion from these experiments is the qualitative one that calcite will melt in the presence of carbon dioxide and water at quite low partial pressures and a temperature around 900 to 1000° C., that is, some three to four hundred degrees below the melting point in the presence of carbon dioxide alone (1340° C. at the dissociation pressure, Smyth and Adams, 1923). It may be noted also that in the presence of water only, at 5000 bars pressure, there is no melting up to 800° C. (Heard 1957).

The melting observed in the presence of water and carbon dioxide in the present experiments is probably the same as that observed by Sir James Hall (1812) in some of his classic experiments during 1798 to 1805. He found that the addition of water greatly helped in obtaining "fusion" of calcium carbonate at temperatures around 1000° C. It would appear that, at least in those experiments in which he intentionally added water, he was not observing fusion to a melt of pure calcium carbonate but rather to one containing water and carbon dioxide (there was also probably CaO present since he found some loss of weight of the $CaCO_3$).

The author is grateful to the Institute of Geophysics, University of California at Los Angeles, and especially to Professor D. T. Griggs and Professor G. C. Kennedy, for the use of their laboratory facilities for these experiments during the summer of 1957, and for many stimulating discussions.

References

Hall, Sir James (1812), Account of a series of experiments showing the effects of compression in modifying the action of heat: *Trans. Roy. Soc. Edinburgh*, **6**, 71–184.

Heard, H. (1957), unpublished experiment.

Smyth, F. H. and Adams, L. H. (1923), The system $CaO\text{-}CO_2$: *J. Am. Chem. Soc.*, **45**, 1167–1184.

THE AMERICAN MINERALOGIST, VOL. 43, MAY–JUNE, 1958

A NEW LOW-TEMPERATURE, LIQUID HEATING STAGE*

William W. Virgin, Jr., and Camillo J. Massoni,
U. S. Geological Survey, Washington 25, D. C.

A new low-temperature, liquid heating stage for the study of liquid inclusions has been designed and constructed at the U. S. Geological Survey. The stage (Figs. 1 and 2) is mounted on the microscope and has an operating range of 30° to 300° C. Features of the heating stage are: (1) a totally immersed mercury thermometer, (2) a three-way adjustable crystal mount that will take a variety of attachments for holding crystals, (3) the accommodation of crystals as much as 3 inches in length, and (4) an easily controllable heating rate.

The basic construction of the heating stage is of a high-temperature resistant material composed of asbestos fibers, diatomaceous silica, and an inorganic binder. The material is light, mechanically strong, and easily fabricated. Aluminum is used as an inside shield and viewing-cell holder on the cover of the stage (Fig. 2A). Clamps for the cover and for securing the stage to the microscope are also made of aluminum. The crystal-mount assembly (B) is made of brass. The heating cell (C) is made from the bottom of a 600 ml. beaker cut to a height of 1¼ inches. An 8-mm. glass tube, 15½ inches long, is fused to the side of the heating cell. This tube is just large enough to allow the passage of a 360° C. mercury thermometer (K) graduated in degree intervals. A stiff wire attached to the thermometer and extending through a cork in the end of the tube permits the thermometer to be moved in and out of the heating cell.

The glass viewing cell (D), 45 mm. outside diameter by 35 mm. deep, was specially made with an optical-glass bottom for maximum visibility. A 50-ml. beaker cut to a height of 35 mm. and ground and polished on

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* Publication authorized by the Director, U. S. Geological Survey.

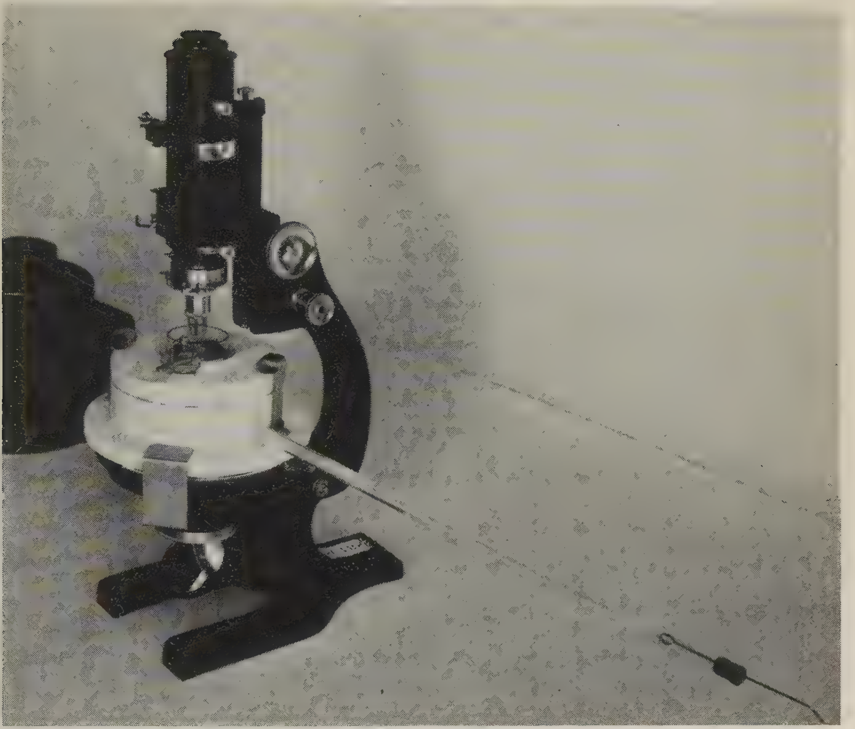

FIG. 1. Liquid heating stage mounted for use.

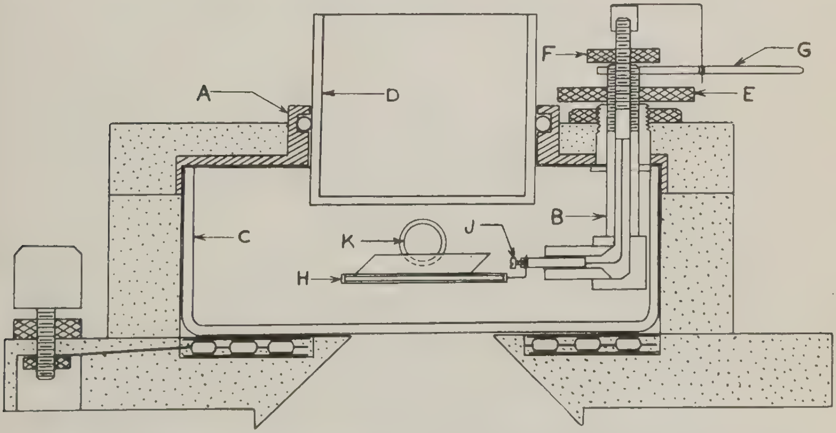

FIG. 2. Cross section of liquid heating stage: (A) viewing cell holder; (B) crystal-mount assembly; (C) heating cell; (D) viewing cell; (E) and (F) adjustable nuts for vertical and north south movements; (G) handle for east-west movement; (H) crystal holder; (J) small screw; (K) thermometer.

both inside and outside of the bottom surfaces to lessen effects of distortion can also be used satisfactorily but does not give the clear, undistorted image obtained with the special cell. The viewing cell is held in place by a rubber ring fitted in the opening of the aluminum part of the cover. Although the viewing cell is held tightly, a little silicone grease on the ring allows vertical adjustment.

The crystal mount is constructed to permit vertical, east-west, and north-south movements. The vertical and north-south movements are controlled by adjustable nuts (E and F) on the crystal positioning mechanism outside the cover, and the east-west movement, in the form of an arc, is controlled by a handle (G) securely attached to the same mechanism. The crystal holder (H) consists of a circular piece of glass held by a brass ring with a small piece of stiff wire attached to the rim of the ring. This unit is fastened to the crystal mount by means of a small screw (J). The size or type of crystal holder can be made to suit the needs of the operator.

The heating medium, essentially tetrachlorobiphenyl, is a colorless liquid used commercially as a heat-transfer medium. It is quite stable, remains essentially colorless during long intervals of heating and has a distillation range of 345° to 385° C. The heating cell holds approximately 125 ml. of this liquid when in use. Although the stage is essentially a closed system, some fumes do appear at temperatures above 200° C. The fumes are toxic and it is advisable to operate the stage under a ventilated hood when working in the range of 200° to 300° C.

The heating element consists of a coil of 2½ feet of no. 20 nichrome wire insulated with ceramic beads (Fig. 2). Two circular pieces of sheet mica with 1½-inch diameter holes, centrally located, are placed above and below the coil in the heating chamber to aid in even heat distribution to the heating cell. The coil is connected directly to a 7½-ampere, 110-volt variable transformer. The rate of temperature increase can be controlled quite easily, or the temperature can be held at any desired point over a period of time.

The accuracy of thermometer readings was checked by the use of melting point standards, organic and inorganic crystals enclosed in small glass tubes, at several points below 285° C. The standards were first checked on a Kofler micro-hot stage.[1] The melting points obtained with both stages are given in Table 1. The close agreement of the results indicates the accuracy to be expected with the liquid heating stage. The variation in temperature across the diameter of the heating cell is less than 1° C. at any temperature below 300° C.

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[1] Cheronis, N. D., 1954, Micro and semimicro methods, Volume VI of Technique of organic chemistry, A. Weissberger, ed.: New York, Interscience Publishers, Inc., pp. 162–168.

Table 1. Comparison of Liquid Heating Stage with the Kofler Micro-Hot Stage

Melting point standard	Kofler micro-hot stage	Liquid heating stage
Vanillin	80.5°– 81° C.	80° – 81° C.
Benzoic acid	122 –123	121.5–122.5
Ammonium nitrate	168 –169.5	167 –169.5
Silver nitrate	209 –213	209 –211
Sodium chlorate	255 –258	254 –258
Anthraquinone	283 –286	282 –285

We wish to thank Joseph F. Abell and Irving Breger, of the U. S. Geological Survey, for their many helpful contributions toward the design and construction of this heating stage. This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

ADDENDUM TO THE PEGMATITE PHOSPHATES

D. Jerome Fisher, *University of Chicago, Chicago 37, Illinois.*

Since the time of the deadline for copy for the paper "Pegmatite Phosphates and Their Problems" (*Am. Mineral.*, **43,** 181) it has been possible to secure samples of rare minerals not previously at hand. The powder diffraction patterns of these appear in Fig. 7. The accompanying table may be considered as an extension of Table 7 of the original paper; all these minerals are there listed in Table 8, except for the recently described hydrous Fe-Mn phosphate *strunzite*, known as fibrous emplacements in cavities from New Hampshire, Maine and Bavaria. Samples A, C–E, G and H are from Professor Frondel, K is from Professor Strunz, and B is from the American Museum of Natural History.

Table 7. Pegmatite Phosphate Powder Diffraction Data

Strongest line	Second line	Third line	Name	Photograph	Locality	Crystal system	*a/b*
2.83	9.0 /8	4.43/7	Phosphophyllite	7A	Hagendorf	M	2.065
2.91	2.18/7	2.97/6	Lacroixite	7B	Saxony	M?	—
3.01	2.81/8	3.49/7	Vashegyite	7C	Nevada	—	—
3.06	3.50/8	2.69/8	Xanthoxenite	7D	N. Hampshire	M?	—
3.10	4.37/8	2.90/7	Palermoite	7E	N. Hampshire	O	.730
3.45	7.3 /8	2.89/8	Väyrynenite	7F	Finland	M?	—
4.18	3.39/8	3.23/7	Parsonsite	7G	N. Hampshire	M	—
7.84	3.95/7	5.82/6	Phosphuranylite	7H	Rumania	O	.910
9.02	5.32/7	3.23/4	Strunzite	7J	N. Hampshire	M	0.543
9.93	6.75/7	3.05/5	Stewartite	7K	Hagendorf	M	.171

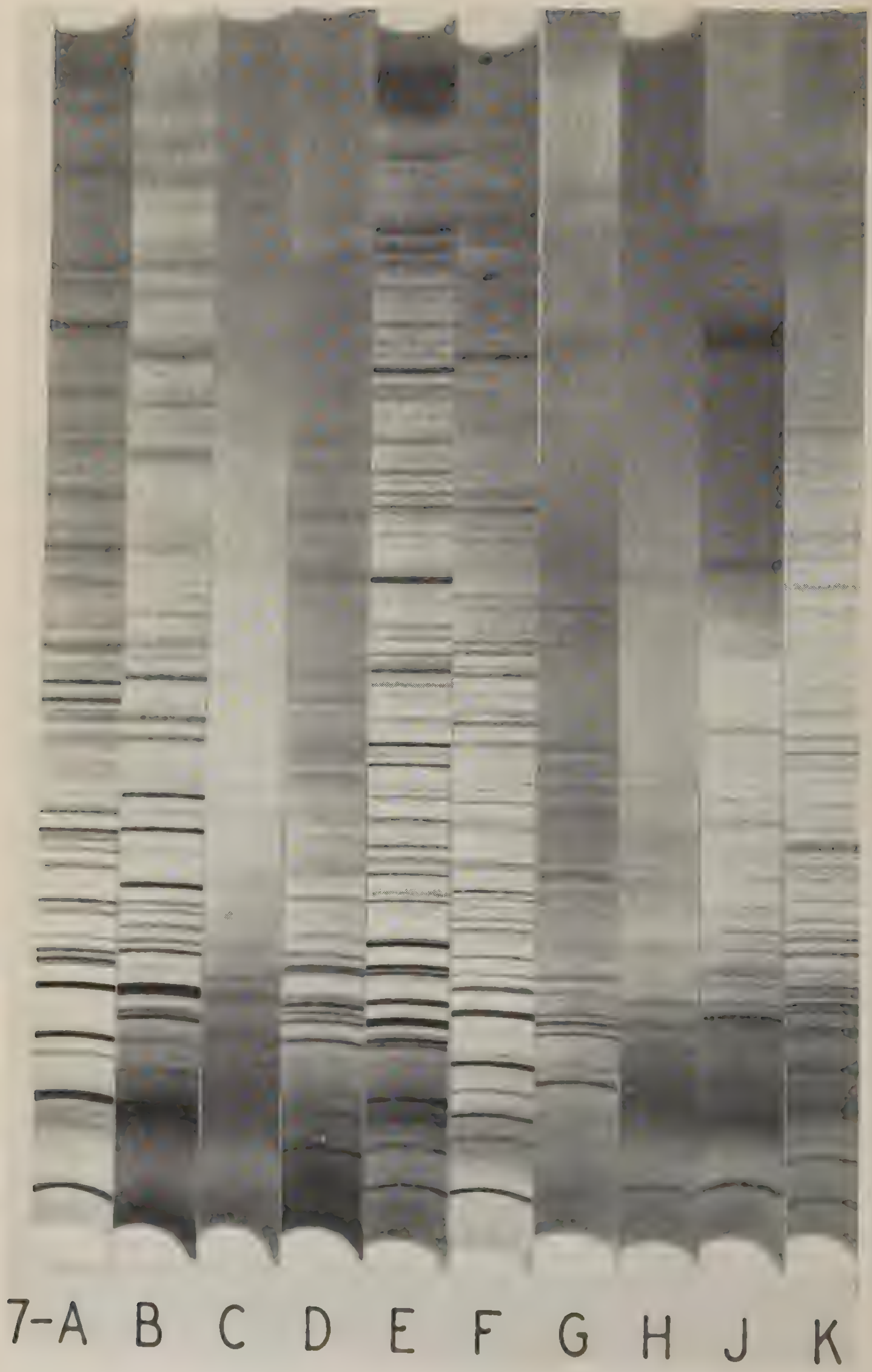

FIG. 7. *X*-ray diffraction patterns of additional pegmatite phosphates.

NOTICE OF ANNUAL MEETING

The thirty-ninth annual meeting of the Mineralogical Society of America will be held in St. Louis, Missouri, Thursday through Saturday, November 6–8, 1958. Detailed notices will be mailed to all members.

Abstracts of papers to be presented at the annual meeting must be received by the Secretary on or before July 15, 1958. Abstract blanks may be obtained from the Secretary.

NOMINATIONS OF OFFICERS FOR 1959

President: R. E. Grim, University of Illinois, Urbana, Illinois

Vice-President: Joseph Murdoch, University of California at Los Angeles, Los Angeles, California

Secretary: C. S. Hurlbut, Jr., Harvard University, Cambridge, Mass.

Treasurer: Earl Ingerson, U. S. Geological Survey, Washington, D. C.

Editor: Lewis S. Ramsdell, University of Michigan, Ann Arbor, Michigan

Councilors (1959–1961):

E. W. Nuffield, University of Toronto, Toronto 5, Canada

W. R. Foster, Ohio State University, Columbus, Ohio

PROPOSED AMENDMENTS TO THE CONSTITUTION

In November, 1956 the President of the Society appointed a committee to consider the constitution and by-laws and suggest changes that would bring them up to date. The committee's report carried many suggested changes, which were debated at length by the Council in November 1957. The proposed revised constitution and by-laws for the Mineralogical Society of America as approved by the Council are printed herewith.

The constitution and by-laws were last printed in 1950 in the *American Mineralogist*, Vol. 35: pp. 611–613, and one should refer to that printing for a complete comparison of the present constitution and by-laws with those proposed. Some of the more important proposed changes in the constitution are:

Wherever *petrography* appeared it is proposed to replace it by *petrology*.

At present the annually elected officers include the Editor. It is proposed that the Editor be appointed annually by the President with Council approval (Art. III, Sec. 2).

The present constitution provides for *Correspondents*. It is proposed to drop this cate gory but add *Honorary Fellows* (Art. IV, Sec. 4).

At present a proposed amendment to the constitution requires that it be favored by four-fifths of the *fellows* voting upon it. It is now proposed that an amendment shall become effective when favored by two-thirds of the *membership* voting upon it (Art. V, Sec. 3).

The by-laws provide at present that the Council shall make nominations for office. In the past only one nomination has been made for each vacancy. It is proposed in the case of nominations for Councillors that there be at least twice as many nominees as there are open positions (by-laws Art. IV).

PROPOSED REVISED CONSTITUTION AND BY-LAWS OF THE MINERALOGICAL SOCIETY OF AMERICA

as approved by the Council, November, 1957

CONSTITUTION

Article I. Name

This Society shall be known as the *Mineralogical Society of America*.

Article II. Object

The object of this Society shall be the advancement of mineralogy, crystallography and petrology, and the promotion of their use in other sciences and in industry.

Article III. Officers

Section 1. The officers of the Society shall be a president, a vice-president, a treasurer and a secretary, who shall be elected annually. There shall be a council consisting of the above officers, the retiring president, and six fellows at large, two of the latter to be elected each year for terms of three years.

Section 2. The editor shall be appointed by the president annually subject to approval by a two-thirds vote of the entire Council.

Section 3. Only fellows are eligible for office.

Section 4. The Council shall be empowered to choose from time to time as honorary officers of the Society persons of eminence in the field of mineralogy who shall serve for life.

Article IV. Membership

Section 1. Membership shall be open to anyone interested in mineralogy, crystallography, or petrology. The general membership shall consist of fellows, members, honorary fellows and patrons.

Section 2. Members shall be persons interested in mineralogy, crystallography or petrology.

Section 3. Fellows shall be members who have contributed significantly to the advancement of mineralogy, crystallography, or petrology, or whose scientific contribution utilized mineralogical studies or data. Fellows are nominated by the Council and elected by the fellows of the Society.

Section 4. Persons who are distinguished for their attainments in mineralogy, crystallography, petrology or allied sciences, may be designated Honorary Fellows by the Council.

Section 5. Persons who have bestowed important favors upon the Society may be designated patrons by the Council.

Section 6. Fellows and members shall be entitled to vote in the transaction of the regular business of the Society.

Article V. Amendments

Section 1. Amendments to the Constitution may be proposed by twenty (20) or more of the membership, at least ten (10) of whom must be fellows. Proposed amendments shall be submitted to the Council at least two months before the annual meeting.

Section 2. Such amendments shall be placed on the ballot the following year for a vote by the membership.

Section 3. An amendment shall go into effect when favored by two-thirds of the membership voting upon it.

BY-LAWS

Article I. Membership

Section 1. Members. Any eligible individual may become a member by submitting an application and paying one year's dues.

Section 2. Election of Fellows. Nominations for fellowship shall be made by three fellows according to a form to be provided by the secretary. Two of these fellows must be personally acquainted with the nominee and his qualifications. The Council shall submit the nominations received, if approved, to a vote of the fellows in the manner provided by the by-laws. The results shall be announced at the next Council meeting, and those elected shall be notified by the secretary.

Section 3. Termination. A member's name will be dropped from the rolls if the annual dues are not paid by January 31.

Article II. Dues

Section 1. The annual dues for members shall be four dollars ($4) payable in January.

Section 2. No person shall be accepted as a fellow of the Mineralogical Society of America unless he pays dues for the year within three months after notification of his election. The annual dues for fellows shall be five dollars ($5) payable in January.

Section 3. Fellows who have reached the age of seventy years, and who have paid dues for at least thirty (30) years, shall be exempt from further payment of dues.

Section 4. An arrearage in payment of annual dues of four months shall deprive a fellow of the privilege of taking part in the management of the Society and of receiving the publications of the Society. An arrearage continuing over (2) two years shall be construed as notification of withdrawal.

Section 5. A single prepayment of an amount equaling twenty times the annual dues of a fellow of the Society shall be accepted as commutation for life for either fellows or members.

Article III. Duties of Officers

Section 1. Officers. The duties of the president, vice-president, treasurer, secretary, and editor of the Society shall be the usual ones performed by such officers. The treasurer, the secretary, and the editor shall make formal reports to the Society at least once a year. These reports shall be published in the journal of the Society.

Section 2. The Council shall direct all affairs and activities of the Society not otherwise provided for by the Constitution as well as perform those duties specifically assigned to it.

Section 3. The president, secretary, and treasurer shall constitute an executive committee.

Section 4. The president shall appoint, with the approval of the Council such committees as may further the objects of the Society, including a board of associate editors.

Article IV. Election of Officers and Fellows

Section 1. (a) Nominations for office shall be made by the Council. For councillors there shall be at least twice as many nominees as there are open positions. Any ten (10) fellows or members may forward to the secretary other nominations for any or all offices. (b) All nominations reaching the secretary not later than three months prior to the annual meeting shall be printed on the ballots to be mailed to the general membership. The results shall be announced at the regular meeting and the new officers shall enter upon duty at the adjournment of the meeting.

Section 2. The list of nominations for fellowship in the Society shall be sent to the fellows at the same time as the nominations for officers. If ten per cent of the fellows voting on a given candidate cast opposing votes, the candidate shall be considered ineligible for fellowship.

Article V. Publications

Section 1. The Society shall publish a journal devoted to the advancement of mineralogy, crystallography, petrology and allied sciences.

Section 2. The general membership of the Society shall receive the journal.

Section 3. Corporations, libraries and institutions may subscribe to the journal at an annual rate to be determined by the Council.

Article VI. Affiliation with Other Scientific Organizations

The Council shall have the authority to arrange for affiliation with other scientific organizations, and, as the occasion may arise, to appoint fellows to represent the Society on the Councils of such organizations.

Artice VII. Local Sections

Local sections of the Society may be formed in any locality, with the advice and consent of the Council, for the purpose of holding meetings and promoting cooperation. The affairs of such local sections shall be entirely in their own hands.

Article VIII. Meetings

There shall be an annual meeting of the Society and such other meetings as may be called by the Council. The annual meeting shall be held, whenever practicable, at the same time and place as that of the Geological Society of America.

Article IX. Revision of the By-Laws

Revision of the by-laws shall be by the procedure established for amendments under Article V of the Constitution except that revision of the by-laws shall be enacted by a simple majority of those voting.

THE SEVENTH NATIONAL CLAY CONFERENCE will be held on October 20 to 23, 1958 in Washington, D. C. at the U. S. National Museum in the Natural History Building of the Smithsonian Institution and will be open to all who have a common interest in clays and clay technology. It is sponsored by the Clay Minerals Committee of the National Research Council and is under the Chairmanship of Dr. H. F. McMurdie of the National Bureau of Standards.

A principal theme for the conference will be "Geology of Clay Deposits." However, papers will also be presented on other phases of the broad subject of "Clays and Clay Minerals." A field excursion is planned for Monday, October 20, to typical clay deposits and soil profiles in northeastern Maryland and northern Delaware. A guided tour to the National Bureau of Standards is being arranged for the afternoon of the 22nd. Complete details of the program will be announced in August.

THE 7TH ANNUAL CONFERENCE ON INDUSTRIAL APPLICATIONS OF *X*-RAY ANALYSIS will be held at the Albany Hotel, Denver, Colorado, on August 13–15, 1958. The Conference chairman is William M. Mueller, Metallurgy Division, Denver Research Institute, University of Denver, Denver 10, Colorado.

Upon the resignation of Dr. G. W. Brindley, Dr. J. V. Smith has been appointed acting editor for the *X-ray Powder Data File*. New data and information concerning errors in the published data are always welcome. Correspondence should be addressed to Dr. J. V. Smith, Mineral Science Building, The Pennsylvania State University, University Park, Pennsylvania.

The first general annual meeting of clay sciences of Japan was held on November 29 30 1957, at the Hall of the National Institute of Agricultural Sciences, Tokyo, under the auspices of the six societies concerning Geology, Mineralogy, Economic Geology, Ceramics, Soil Sciences, and Chemistry. 35 papers were read. Among them, 7 papers concern somewhat longer survey lectures on subjects of general interest: wall rock alteration, laterite, soil clay minerals, crystal chemistry, acid clays and activated clay, electron microscopy, and clay-water relationship. Other subjects cover all the fields of interest of the above societies. All of the papers read in this meeting will be published as a book at the end of 1958.

At the end of November, 1958, the second general annual meeting of clay sciences of Japan will be held in Tokyo. Those who hope to make suggestions concerning the book and also the forthcoming meeting in 1958 should write Dr. T. Sudo, Geological and Mineralogical Institute, Faculty of Science, Tokyo University of Education, Otsuka, Bunkyo-ku, Tokyo, Japan.

The Davy Medal of the Royal Society (London) has been presented to Dame Kathleen Lonsdale, professor of chemistry at the University College, London, for her distinguished studies in the structure and growth of crystals.

THE GROTH INSTITUTE at Pennsylvania State University

The Pennsylvania State University announces the establishment of *The Groth Institute*, in its College of Chemistry and Physics, under the direction of Ray Pepinsky, Research Professor of Physics and Director of the *X*-Ray and Crystal Structure Laboratory. Prof. John A. Sauer, Head of the Department of Physics, will serve as the University's administrative representative in the *Institute.*

Purpose of the Institute

The purpose of *The Groth Institute* is to serve as the world center for revision of the encyclopedia of crystal chemistry and physics entitled *Chemische Krystallographie*, issued by the great German crystal chemist, physicist and mineralogist, Prof. Paul Heinrich Ritter von Groth, between the years 1906 to 1919. Groth's compilation of crystal properties is still of tremendous value to science and technology; but it was conceived before the discovery of *x*-ray diffraction and crystal structure analysis, and therefore contains very little information, compared to that now available or developable, relating crystal structures and chemical and physical properties. Discussion of all known relationships of this type, deductions of new relations, and revelation of the most important gaps in knowledge in this realm, are among the first purposes of the new encyclopedia. Advances in older and development of many entirely new types of physical measurement since the first compilation, and consequent accumulation of data, further necessitate revision. Finally, very many new compounds have been prepared and crystallized since Groth's time, and many measurements made on these as well as on older materials.

ERRATUM

In the paper on "Some properties of diamond" in the January–February, 1958 issue of the *American Mineralogist*, there is an error in the third line on page 106. The word "only" should read "except."

BOOK REVIEWS

PHYSICS AND CHEMISTRY OF THE EARTH. Vol. I, 317 pp. (1956), 55 shillings; Vol. II, 259 pp. (1957), $10.00. Pergamon Press, London and New York.

These volumes are the first of a series to be published annually. The foreword states, "The principal aim . . . will be to provide authoritative and up-to-date surveys of progress for those actively engaged in geophysics and geochemistry. But it is to be hoped also that much of what is written will encourage the interest of the chemist and physicist in a study of our planet, not merely for its own sake, but because such a study often turns out to be of benefit to physics and chemistry. Another aim is to acquaint the geologist with the results and methods of geophysics and geochemistry, particularly as progress in earth science has been hindered by some lack of liaison between different groups."

The contents of the two volumes are:

Volume I

The origin of the solar system. Sir Harold Spencer Jones, pages 1–16.
Temperatures within the earth. J. Verhoogen, pages 17–43.
Radioactive methods for determining geological age. L. H. Ahrens, pages 44–67.
Seismology and the broad structure of the earth's interior. K. E. Bullen, pages 68–83.
The hydrodynamics of the earth's core. Raymond Hide, pages 94–137.
Investigations under hydrothermal conditions. Rustum Roy and O. F. Tuttle, pages 138–180.
The geochemistry of the halogens. Carl W. Correns, pages 181–233.
Geochemistry in the U.S.S.R. (1948–1953). S. I. Tomkeieff, pages 235–284.

Volume II

An experimental approach to problems in physical oceanography. William S. von Arx, pages 1–29.
A survey of the quality of some of the principal abundance data of geochemistry. L. H. Ahrens, pages 30–45.
Boundary conditions for theories of the origin of the solar system. Harold C. Urey, pages 46–76.
Some current aspects of chemical oceanography. Francis A. Richards, pages 77–128.
Recent geophysical exploration of the ocean floor. M. N. Hill, pages 129–163.
The geochemistry of gallium, indium, thallium—a review. Denis M. Shaw, pages 164–211.
Latitude variation. P. J. Melchior, pages 212–243.

The board of editors, L. H. Ahrens, K. Rankama, and S. K. Runcorn for volume I, and the same plus Frank Press for volume II, have assembled two volumes that meet the aims set forth. Many of the articles are of evident interest to mineralogists; the unwary reader may find himself fascinated by a review of something outside his normal field of interest, as I was, for example, by the paper by von Arx. Both volumes are highly recommended.

MICHAEL FLEISCHER
Washington, D. C.

MANUAL OF THE POLARIZING MICROSCOPE, by A. F. HALLIMOND, reprint of the second edition of 1953 with additions and minor corrections. 219 pp., Cooke, Troughton and Simms, Ltd., York, England, 1956.

A detailed review of the second edition of this book appears in volume 39 of this *Journal* on pages 845–846. The 1956 reprint edition contains minor corrections and two new appendices. In preparing this reprint, some confusion is introduced into the numbering of the figures. The figure on page 184 is unnumbered. Figure 93 is assigned to an illustration on page 190 and to another on page 202.

Appendix 5, entitled, "Preparation of Polished Sections," consists of six pages and one figure. It is a supplement to Chapter 18 and it takes into account the recent developments in polishing techniques which have improved the quality of the polished surface and reduced the time necessary to produce it. There is a detailed discussion of the use of norbide and sized diamond dust as abrasives, and of the use of nylon and other materials as surfaces for laps. Mention is also made of polished thin sections.

Appendix 6 treats the "Point Counter." The emphasis is on the I. H. Ford point counter. A curious error appears in this section where the Wentworth-Hunt instrument for thin section analysis is stated to be a variant of the Leitz, six-spindle stage described by K. H. Scheumann (1931). This arises from a reversal of the date of publication of Hunt's paper given as 1942. Professor Hunt's paper actually appeared in 1924.

Two color plates are a welcome addition to this book. They contain 18 colored figures, consisting of the spectrum, the spectrum of an interference color in a higher order, the quartz wedge, the quartz wedge in red light, pleochroism of penninite, 4 figures of thin sections, a quartz fragment between crossed polars, and six excellent interference figures.

Mineralogists, petrographers, economic geologists, and microscopists will find much of value to them in this book.

George T. Faust
Washington, D. C.

THE DIFFERENTIAL THERMAL INVESTIGATION OF CLAYS. Edited by Robert C. Mackenzie with contributions by twenty-two authors. 456+xii pp., 99 figures. Mineralogical Society, 41 Queen's Gate, South Kensington, London, S.W. 7, 1957. Price $9.00.

This book is the sequent volume to the monograph *X-Ray Identification and Crystal Structures of Clay Minerals* published by the Mineralogical Society. The title is somewhat misleading as to the scope of this book in that DTA (differential thermal analysis) curves and references to the literature are given for a fairly large number of non-clay group minerals. The book is well illustrated and although there are only 99 figures listed as such, almost every figure is made up of several parts or contains two or more thermal analysis curves. There are 26 TGA (thermogravimetric analysis) curves, 18 weight loss (or dehydration) curves, and about 410 complete, or reasonably complete, DTA curves.

The chapter titles and the authors are as follows:

I. Thermal Methods
    by R. C. Mackenzie
II. Apparatus and Technique for Differential Thermal Analysis
    by R. C. Mackenzie and B. D. Mitchell
III. Theory and Quantitative Use
    by E. C. Sewell and D. B. Honeyborne
IV. The Kaolin Minerals (Kandites)
    by D. A. Holdridge and F. Vaughan
V. The Montmorillonite Minerals (Smectites)
    by R. Greene-Kelly
VI. The Mica Minerals
    by M. Munoz Taboadela and V. Aleixandre Ferrandis
VII. The Vermiculite Minerals
    by G. F. Walker and W. F. Cole
VIII. The Chlorite and Serpentine Minerals
    by S. Caillere and S. Henin

IX. The Sepiolite and Palygorskite Minerals
by S. Caillere and S. Henin
X. Clay Mineral Mixtures and Interstratified Minerals
by W. F. Cole and J. S. Hosking
XI. The Silica Minerals
by R. W. Grimshaw and A. L. Roberts
XII. The Oxides of Iron, Aluminum and Manganese
by R. C. Mackenzie
XIII. The Carbonate Minerals (with some notes on calcium and magnesium hydroxides)
by T. L. Webb and H. Heystek
XIV. Other Minerals
by R. J. W. McLaughlin
XV. Differential Thermal Analysis using Controlled Atmosphere
by E. C. Jonas and R. E. Grim
XVI. Carbonaceous Materials
by R. W. Grimshaw and A. L. Roberts
XVII. Practical Applications
by R. H. S. Robertson

Seventy-nine pages of the book, chapters I, II, and XV, are devoted to the history, apparatus, limitations, and interpretation of DTA methods per se. Some information is also given for TGA and other methods of thermal analysis. The theory of DTA and of the quantitative methods is discussed in thirty-three pages. The rest of the book deals with the DTA, and to a lesser extent TGA, and dehydration curves of minerals and carbonaceous materials. The differential thermal analysis of the clay minerals is treated in great detail and special techniques and methods of interpretation of the data are given. The nomenclature of the clay minerals in this book is not satisfactory.

The book is well documented with references, including those to the Slavic literature. It is a mine of information and all workers in thermal analysis will be grateful to the authors and the editor for their efforts. *The Differential Thermal Investigation of Clays* deserves the attention of all students in this field.

George T. Faust
Washington, D. C.

LABORATORY MANUAL OF CRYSTALLOGRAPHY FOR STUDENTS OF MINEROLOGY AND GEOLOGY, by George Tunell and Joseph Murdoch. Wm. C. Brown Company, Dubuque, Iowa, 1957; lithoprinted, in paper covers, 55+v pages. A 14 cm. stereographic net is included in a pocket.

The *Laboratory Manual of Crystallography for Students of Mineralogy and Geology* is intended to supplement the standard textbooks in mineralogy, containing a more thorough treatment of geometrical crystallography than is usually given.

In the first chapter of the manual, the concept of vector properties of crystals as related to symmetry is introduced. Elements of symmetry, including axes of rotary reflection, are described. The equivalence of symmetry elements is schematically shown.

The following four chapters contain a description of the use of the contact goniometer; definition of zones; treatment of the law of rational intercept ratios, Miller indices, and zone indices; and a brief explanation of the stereographic projection and crystal classes and systems.

Chapter VII, "Crystal Forms in the 32 Crystal Classes," follows, for the most part, the logical nomenclature of Federov and Groth as modified by Rogers. A number of alternative form names are given in the tabulation, for example, monohedron for pedion. The authors seem to prefer the term dihedron for both the dome and sphenoid, although the alternative terms are given. To the reviewer this seems an unfortunate choice. Form names are given for the seven types of Miller indices for each of the crystal classes. Table 8 in Chapter VIII, "Summary of the 32 Crystal Classes," gives a stereographic and axonometric projection (orthographic on an inclined plane) of the general form for each class. A notable feature of these illustrations is that the stereographic projection truly represents the specific general form illustrated. The crystallographic elements, direct and polar, including those fixed by symmetry, are listed. The choice of reference axes with respect to symmetry is indicated. The indices of all of the faces of the general forms are given, including those for alternate settings.

The calculation of axial angles is described in Chapter IX. In this chapter the use of the gnomonic projection and polar lattice are introduced as an aid to indexing crystals. The use of crystallographic data in relation to other properties of minerals, as applied to mineral identification, is explained in the last chapter.

The appendix is a list of minerals arranged alphabetically under crystal class and system. Crystals whose classes have not been determined uniquely are appropriately indicated. For each system a list of minerals—undifferentiated with respect to class is included.

The detailed summaries in Chapters VII and VIII constitute a valuable recapitulation of the geometrical features of the 32 crystal classes. The manual should be useful in teaching elementary crystallography to undergraduate students of mineralogy and geology.

Reynolds M. Denning
University of Michigan
Ann Arbor, Michigan

MINERALOGISCHE TABELLEN, Eine Klassifizierung der Mineralien auf kristallchemischer Grundlage, Dritte Auflage, by Hugo Strunz. 448+x pp., illustrated. Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig, 1957. DM 34.– ($10.30).

The latest edition of this most useful work represents an increase in size of the volume by approximately one-half over the second edition, which appeared in 1949, despite the concise tabular arrangement of the data. A new and valuable addition in this revision is the index of formulas which comprises 19 pages. It now appears in a full cloth binding.

Strunz's "Mineralogische Tabellen" represents, in outline form, the composite information obtained through a crystal-chemical approach to mineralogy. How significant the progress in mineralogical science has been becomes apparent upon comparison of "Mineralogische Tabellen" by P. Groth and K. Mieleitner, published in 1921, with the present volume.

To the general discussion of crystallographic and crystal-chemical principles (part I) has been added a table of ionic radii of Goldschmidt, of Pauling, and of Ahrens. Although most of the figures are the same as those previously used, portions of the text have been completely rewritten.

The use of "klinovariscit" (metavariscite) and "klinostrengit" (phosphosiderite) is consistent with the dubious principle of changing names for the sake of making changes—an innovation introduced into "Dana's System of Mineralogy" by Frondel, except that the latter author uses "metastrengite," an even less justifiable synonym for phosphosiderite. Other criticisms seem superfluous.

This latest edition of this most outstanding summary treatment of crystal-chemical mineralogy deserves extensive utilization on the part of American mineralogists; Strunz's book falls in the "essential" category.

Duncan McConnell
Ohio State University
Columbus, Ohio

X-RAY CRYSTAL STRUCTURE, by DAN MCLACHLAN, JR., pp. xiii+416. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y., 1957. Price $15.00.

The purpose of this book is set forth in the opening sentences of its preface: "Many books have been written in a *popular* style to emphasize the importance of x-ray crystallography and to create interest in the wonderful findings of the workers in the field. A few books have been written with *rigor* for the benefit of the most advanced scholars. In between the extremes of *popular* and *rigorous* there is a gap. As a consequence of this gap, a very large proportion of the x-ray crystallographers actively engaged in the field in America today are working out structures successfully only because they have bridged the gap by having read a necessarily large number of those papers in the scientific journals which serve as signposts for the theory and the proper procedure. It is the purpose of the present text to furnish a common source in which the student may find condensed the teaching of the pioneers in crystallography."

This aim the author has sought to accomplish in nine chapters and an appendix. Every chapter is flavored by the author's own style and approach. This seems refreshing in places but the author is clearly an impatient man. Many subjects are barely touched upon and the reader is repeatedly advised to make a "study of the literature" or "urged to consult" original sources. If he follows these suggestions he will have to read a "necessarily large number of those papers.

The first chapter of 23 pages, entitled "Crystals," opens with a brief historical account in which crystallography up to 1912 is treated with more than the usual contempt which it meets in some circles. Not even Fedorov is mentioned. In this chapter one may read that "there are 230 space groups among crystals, all identifiable by the occurrence of absences or extinctions" and that "these 14 lattices are often called Bravais lattices because of his discovery of them by optical means." The point groups are enumerated in this chapter and each is illustrated by a stereographic diagram showing the distribution of planes of the general form and by a crystal drawing. Some of these drawings suggest that there has been a decline in the "art of pictorial representation" which is said to have been "well advanced" before 1912. The stereographic diagram for the point group $\bar{3}$m shows only 6 points representing the general form.

The second chapter, "Point Groups and Space Groups" (53 pages), is largely devoted to the derivation of the point groups in an elegant manner. This leads to their description in terms of "functional symbols." These symbols are tabulated together with the Schoenflies and International symbols but both of the standard schemes of symbolism remain unexplained. The point groups are again shown in diagrams, this time in pictures of general sets of points in space groups having primitive lattices and no symmetry elements with translation components, from *P*1 to *Pm3m* as it were. Only 12 pages are devoted to space groups, about half this space being occupied by a table. The legend of Fig. 2-9 reads "The transformation inferred by a mirror."

The third chapter, "Crystals and the Application of X-rays" (55 pages), includes descriptions of the principal methods for recording *x*-ray diffraction from single crystals. The emphasis does not correspond at all to the present importance of the several methods. Seven pages are devoted to "The Laue Camera and Gnomonic Projections." Fig. 3-26, which is intended to show the reciprocal-lattice interpretation of Laue diffraction patterns, is marred by faulty construction. The Schiebold Sauter camera is allotted 4 pages, double the space given to the precession camera.

"The Determination of Space Groups" by *x*-ray diffraction is briefly and partially explained in the 19 pages of chapter 4. Extinction rules are set forth in a table, but since the structure factor equation has not been stated, their derivation is only vaguely hinted. No mention is made of Laue groups, of the nature of the ambiguities that may arise, nor of the auxiliary data and considerations that may be involved in the determination of space groups. Over half of the chapter is occupied by two painfully detailed reports of student's exercises in space group determination.

In chapter 5, "The Scattering of X-rays" (44 pages), much space is devoted to basic concepts before the crucial matters of "structure factors of atoms" and "structure factors for crystals" are treated. Brief reference is made to "structure factors of molecules" and the chapter closes with a discussion of certain of the corrections to be considered in utilizing measured intensities. Chapter 6 (23 pages), on "The Nature and Properties of Fourier Series" lays the groundwork for the chapter which follows. All that the author has to say about crystal structure determination is contained in the 50 pages of chapter 7 on "The Phase Problem in Structure Determination." Though this may be considered the key problem of contemporary crystallography, the procedures of crystal structure determination are presented in a rather one-sided manner when discussed only as methods of solving this problem. Many crystal structures, even some intricate structures, have been solved by ingenious methods in which the phase problem was not explicitly involved. The chapter does contain a section on "the trial method" but hardly a suggestion is given of the many ways in which trial structures have been obtained. This is followed by sections on the use of heavy atoms and isomorphous pairs, the Patterson summation and means of its interpretation, and finally several sections on inequalities and other recent developments ending in 15 pages on the Karle-Hauptman method and its evaluation.

Chapter 8 (54 pages), on "Computing Aids in Structure Determination," begins with a discussion of the strip methods and continues with discussions of most, if not all, of the various optical, mechanical and electronic devices which have been used for facilitating crystallographic computation.

In the ninth and final chapter, 60 pages are devoted to "Examples of Structures Which Have Been Determined." The first two examples, those of TiN and tetraphenylmethane, are taken from student's theses. Equation (9-6) gives the structure factor formula for TiN, which has halite structure as $F_{hkl}=4(f_{\mathrm{Ti}}+f_{\mathrm{N}})$. Other structure determinations discussed are those of resorcinol, phthalocyanine, hexamethylene diamine dihydrochloride, trimethylamine sulfur trioxide and a hypothetical structure chosen to clarify the method of shifted Patterson products.

The appendix of 15 pages on "Special Recording Techniques" is devoted to "the gyrating Laue camera," "recording of x-ray diffraction patterns on spheres," the mechanical "transformation of Weissenberg pictures to undistorted theta lattices" and to "divergent beam pictures."

Throughout the style is highly personal and much emphasis is laid on curious or even trivial methods and devices which have caught the author's fancy. Though some sections are heavily weighted with mathematics, the brief section entitled "Stereographic projections" lacks exact statement of the derivation or properties of this projection and it is used solely for showing point group symmetry. It is to be expected that little space should be given in this book to diffraction by polycrystalline material, but it is surprising to find that little space devoted to the photographic recording of "Debye-Scherrer circles" on a sphere. It seems unlikely that this book will render obsolete the excellent British texts on the interpretation of *x*-ray diffraction photographs and the determination of crystal structures.

A. Pabst
University of California
Berkeley, California

STRUCTURE REPORTS FOR 1951. Vol. 15. General Editor A. J. C. Wilson; Section Editors: N. C. Baenziger (Metals), J. Wyart (Inorganic Compounds), J. Monteath Robertson (Organic Compounds). Published for the International Union of Crystallography. N. V. A. Oostheok's Uitgevers Mij., Utrecht, Holland. viii+588 pp. (1957). Price 110.—Dutch florins; £10.10.0; $29.00.

Those already familiar with these reports have eagerly awaited this volume. For those not familiar, it should be stated that they offer a very complete coverage of crystal structure data. These data are given in adequate detail, while non-structural portions of papers are not abstracted. Editorial comment, and in some cases corrections, are valuable features.

Volume 14, consisting of cumulative indices for 1940–1950, is now in preparation.

REYNOLDS M. DENNING
University of Michigan
Ann Arbor, Michigan

SNOW CRYSTALS, NATURAL AND ARTIFICIAL, by UKICHIRO NAKAYA. 510 pages. Harvard University Press, Cambridge, Mass., 1954. Price, $10.00.

Dr. Nakaya, now Professor of Physics at Hokkaido University, has made a lifetime study of snow crystals, natural and artificial, having begun this fascinating study in 1932. This book is a summary of the work done by Professor Nakaya and his colleagues. Today they are able to produce every type of natural snow crystal in the laboratory and have determined, in almost every case, the conditions of their formation.

The book is divided into the following chapters:

Part I: Natural Snow
  Chapter 1. Observation of Snow Crystals
  Chapter 2. General Classification of Snow Crystals and Their Frequency of Occurrence
  Chapter 3. Physical Properties of Snow Crystals

Part II: Artificial Snow
  Chapter 4. Artificial Production of Frost Crystals
  Chapter 5. Artificial Production of Snow Crystals
  Chapter 6. Investigations on Artificial Snow
  Chapter 7. Comparison of Natural and Artificial Snow Crystals
  Chapter 8. Recent Researches on the Formation of Snow Crystals
  Appendix. Classification of Snow Crystals for Practical Purposes

Bibliography and References

Plates

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In addition to the 197 pages of plates at the end of the book showing photomicrographs of snow crystals, each chapter is most generously illustrated with additional photomicrographs and sketches of snow crystals.

The photomicrographs in general are very clear. The book is printed on good paper and is well bound in a hard black cover, and measures 10 inches by 7 inches.

There is a wealth of written information on the formation of snow crystals, but its great value to the average mineralogist, geologist, student and to the layman lies in the illustrations. This book is a must for every school and departmental library and would enrich the library of anyone interested in mineralogy.

JEROME H. REMICK
University of Michigan
Ann Arbor, Michigan

NEW MINERAL NAMES

Cadmoselite

E. Z. BUR'YANOVA, G. A. KOVALEV, AND A. I. KOMKOV. The new mineral cadmoselite. *Zapiski Vses. Mineralog. Obshch.*, **86**, 626–628 (1957) (in Russian).

The new mineral was found as fine xenomorphic disseminations cementing sandstone (locality not given) associated with ferroselite, clausthalite, amorphous selenium, cadmian sphalerite, and pyrite. Microchemical tests gave strong tests for Se and Cd, a weak test for S, and no test for Zn. The presence of Cd and the absence of Zn were confirmed spectrographically.

X-ray study showed the mineral to have the wurtzite structure. An indexed *x*-ray powder pattern is given and leads to a cell with a_0 4.262 ± 0.003, c_0 6.955 ± 0.005 kX. Comparison with published data for synthetic CdS and CdSe indicates that the composition is approximately $Cd\,(Se_{0.85}S_{0.15})$. The strongest lines are 2.13(10), 1.816(8), 3.67(7), 1.196(7), 1.020(7), 1.443(6).

The mineral is black with black streak, luster resinous to adamantine. Hardness medium; very brittle. Cleavage perfect, apparently prismatic. Crystals show the base and the haxagonal pyramid, the latter with horizontal striations. In immersion black and opaque; in reflected light gray, somewhat lighter than sphalerite; shows weak brownish tint in oil immersion. Polarizes weakly with crossed Nicols in oil immersion.

The name is for the composition.

MICHAEL FLEISCHER

Santafeite

MING-SHAN SUN AND R. H. WEBER. Santafeite, a new hydrated vanadate from New Mexico. *Bull. Geol. Soc. Am.*, **68**, 1802 (1957) (abs.).

The mineral has the formula $Na_2O.6(Mn,Ca,Sr)O \cdot 3\,MnO_2 \cdot 3(V,As)_2O_5 \cdot 8H_2O$ (analysis not given). Readily fusible in an alcohol flame to a dull black bead. It occurs as an incrustation in small rosettes of acicular crystals on a joint surface of limestone in the Grants uranium district, McKinley County, New Mexico. Color black, streak brown, luster subadamantine. Translucent only in very small fragments, pleochroic from dark reddish brown to yellowish brown, with absorption $X > Y > Z$, $X = c$, alpha = 2.01, distinct dispersion. *X*-ray study shows it to be orthorhombic, space group $V^{11}{}_h - Pmca$ with a_0 9.26, b_0 30.02, c_0 6.28, all ±0.02 Å. Cleavage (010) perfect, (110) distinct.

The name is for the Atchison, Topeka, and Santa Fe Railroad Co., "in recognition of its pioneer exploration and development of the uranium deposits in New Mexico."

DISCUSSION: The mineral has no close analogies; perhaps to be placed in Class 42 of Dana's System, 7th Ed., Vol. II. This mineral was first erroneously identified as ardennite (*Am. Mineral.*, **40**, 338 (1955)).

M. F.

Horobetsuite

KITARO HAYASE, Minerals of bismuthinite-stibnite series with special reference to horobetsuite from the Horobetsu Mine, Hokkaido, Japan. *Miner. Jour.* (*Miner. Soc. Japan*), **1**, 189–197 (1955).

Horobetsuite occurs in the sulfur deposit of Horobetsu Mine, associated with free sulfur and iron sulfide minerals. Crystal habit prismatic with striations parallel to the prism zone. Size 1.0 7.0 mm. in length, and 0.2–2.0 mm. in diameter. Sp. gr. 5.449 (at 20° C.), hardness ca. 2, color lead gray, streak black, interference color pale yellow-gray-dark brown, pleochroism very pale brown-pale blue, not distinct, parallel extinction. Unit cell $a_0 = 11.24$ Å, $b_0 = 11.28$, $c_0 = 3.90$.

Chemical composition:

	Bi	*Sb*	*S*	*Fe*	*Insol.*	*Total*	*Anal.*
No. 1	56.93	21.49	21.57	tr.	tr.	99.99	S. Ito
No. 3	44.80	32.30	23.00	tr.	0.05	100.15	S. Ito
No. 3	51.84	17.20	24.15	5.20	0.98	99.37	R. Sei

Chemical formula of horobetsuite is determined as (Bi, Sb)$_2$S$_3$, where mol. ratio of $Bi_2S_3:Sb_2S_3$ varies between 9:11 and 13:7. Etching test 1:1 HNO_3—Stains brownish black; same with 1:1 HCl, 5% $HgCl_2$ and 20% $FeCl_3$; 40% KOH—Etching begins within 9–300 sec., stains brown; 20% KCN—Etching begins within 35–85 sec., stains brown.

The data above mentioned show the mineral is a new species, intermediate between bismuthinite and stibnite in physical as well as chemical properties. Therefore a new name, horobetsuite, is proposed for the mineral of the bismuthinite-stibnite series, which has mol. ratio of $Bi_2S_3:Sb_2S_3$ between 7:3 and 3:7. The name is for the mine, where the mineral has been found for the first time.

KENZO YAGI

Bruyerite

G. TACNET. Bruyerite. *Soc. Hist. Nat. Creusot*, **14,** No. 4, 1956, in *Fed. franc. soc. sci. nat.* No. 5, Oct., 1956.

The name bruyerite is given to black concretionary material found at Queue de Bruyère, Breuil Reservoir, near Le Creusot, central France. It contains also quartz and mica and is apparently one of the final stages in the transformation of green marl to indurated rock. Chemical, optical, and *x*-ray data (not given) indicate it to be calcite, probably of organic origin.

MARJORIE HOOKER

Rhodesite, Mountainite

E. D. MOUNTAIN. Rhodesite, a new mineral from the Bultfontein mine, Kimberley. *Mineralog. Mag.*, **31,** 607–610 (1957).

J. A. GARD, H. F. W. TAYLOR, AND R. A. CHALMERS. An investigation of two new minerals: rhodesite and mountainite. *Mineralog. Mag.*, **31,** 611–623 (1957).

The minerals occur as matted silky white fibers in rosettes up to 2 mm. in size, strongly resembling natrolite. *X*-ray and optical study showed that two minerals were present.

Analyses 1, 2 by E. D. M. on air-dried material, 3 and 4 by R. A. C., 1–3 rhodesite, 4 mountainite; 1 after fusion, 2 after decomposition with HCl.

	1	2	3	4
SiO_2	61.79	61.86	61.6	58.5
Al_2O_3	0.30	0.28	nil	nil
FeO	0.25	0.25	nil	n.d.
CaO	14.95	14.85	15.1	13.4
MgO	0.09	0.07	nil	0.2
Na_2O	5.04	4.82	5.2	7.9
K_2O	5.40	5.16	6.0	6.0
H_2O	12.45	12.55	12.3[a]	13.4
	100.27	99.84	100.2	99.4

[a] Total loss on ignition; may include a little CO_2. Mountain states, "Chemical tests on other samples suggest that the lime can be as high as 18%, and the alkalis correspondingly low."

These correspond approximately for rhodesite to $4(Ca, Na_2, K_2)O.10SiO_2\cdot 7H_2O$ with $Ca:(Na_2+K_2)=2:1$ (Mountain), or $(Ca, Na_2, K_2)_8Si_{16}O_{40}\cdot 11H_2O$ (G., T., and C.) and for mountainite to $(Ca, Na_2, K_2)_{16}Si_{32}O_{80}\cdot 24H_2O$, with $Ca:(Na_2+K_2)$ nearly 1:1.

D.T.A. curves by R. C. Mackenzie show for rhodesite and mountainite large endothermic breaks at 345° and 332°, respectively, small endothermic breaks at 735°, and a small exothermic break at 960°. Mountain states that rhodesite lost 4.14% H_2O at 110° and the sample regained all the water in 12 hours at room temperature. Heating at 275° drove off practically all the water, and all but 1% of it was recovered in 8 hours at room temperature. Gard and Taylor found no difference in the *x*-ray pattern of rhodesite heated at 500°. On ignition it melted to a glass that gave a weak pattern of pseudo-wollastonite. They found no change in mountainite heated at 160°; material heated at 275° and 400° gave weak patterns; that heated at 1000° melted to a glass that gave a weak pattern of β-$CaSiO_3$.

Rhodesite gave *ns* α 1.502, β 1.506, γ 1.515 (EDM), α 1.502, β 1.505, γ 1.515 (G. and T.), probably positive with low 2V, $\alpha=b$, $\beta=a$ (normal to cleavage), $\gamma=c$ (elongation). Mountainite has α 1.504, β 1.510, γ 1.519, probably positive with moderate or high 2V, $\beta=b$ (elongation), G. for rhodesite about 2.36 (M.), 2.36 (G., T., and C.), for mountainite 2.36 (G., T., and C.)

Rhodesite is orthorhombic with $a=23.8$, $b=6.54$, $c=7.05$ Å.; the unit cell contains $(Ca, Na_2, K_2)_8Si_{16}O_{40}\cdot 11H_2O$. Cleavage (100) good. Electron microscope and electron diffraction patterns (G. and T.) correspond to $a=25$, $b=6.57$, $c=7.00$ Å, with some indication of a superlattice with *a* and *b* doubled. Mountainite is monoclinic with $a=13.51$, $b=13.10$ (or possibly 6.55), $c=13.51$ Å, β 104°; the unit cell contains $(Ca, Na_2, K_2)_{16}Si_{32}O_{80}\cdot 24H_2O$.

Indexed *x*-ray powder patterns are given for both minerals; the strongest lines are: Rhodesite, vs 3.07, s 11.8, 6.56, 3.02, 2.89, 2.78; Mountainite, vvs 2.94, vs 6.6, s 13.1, 4.67, ms 2.80, 1.967.

The general similarity of the two minerals to the fibrous zeolites, such as thomsonite and gonnardite, is discussed. They differ markedly from these in the absence of aluminum.

The names are for Cecil J. Rhodes, and for Edgar D. Mountain, professor of geology at Rhodes University, Grahamstown, Union of South Africa, Rhodesite is pronounced rōdzīte.

Michael Fleischer

Tri-kalsilite

T. G. Sahama and J. V. Smith. *Am. Mineral.*, **42,** 286 (1957).

Smythite

R. C. Erd, H. T. Evans, Jr., and D. H. Richter. *Am. Mineral.*, **42,** 309–333 (1957).

Duttonite

M. E. Thompson, H. Roach, and Robert Meyrowitz. *Am. Mineral.*, **42,** 455–460 (1957).

Ferroanthophyllite (aluminian)

Yotaro Seki and Masao Yamasaki. *Am. Mineral.*, **42,** 506–520 (1957).

Doloresite

T. W. Stern, L. R. Stieff, H. T. Evans, Jr., and A. M. Sherwood. *Am. Mineral.*, **42,** 619–628 (1957).

Nolanite

S. C. Robinson, H. T. Evans, Jr., W. T. Schaller, and J. J. Fahey. *Am. Mineral.*, **42,** 619–628 (1957).

Un-named lead germanium sulfate

Clifford Frondel and Jun Ito. *Am. Mineral.*, **42,** 743–753 (1957).

Bikitaite

C. S. HURLBUT, JR. *Am. Mineral.*, **42,** 792–797 (1957).

M. F.

NEW DATA

Bismutoferrite, Chapmanite, Hypochlorite

CHARLES MILTON, J. M. AXELROD, AND BLANCHE INGRAM. Bismutoferrite, chapmanite, and "hypochlorite," *Bull. Geol. Soc. Am.*, **68,** 1769 (1957) (abs.).

Bismutoferrite (Frenzel, 1871), hitherto considered to be a mixture (Dana's System, 6th Ed., p. 562) is found by *x*-ray and chemical study to be a valid mineral of composition $BiFe_2(SiO_4)_2(OH)$ or $Bi_2O_3 \cdot 2Fe_2O_3 \cdot 4SiO_2 \cdot H_2O$. It is isostructural with chapmanite (Walker, 1924) (*Am. Mineral.*, **10,** 41 (1925)), whose formula is therefore revised to $SbFe_2(SiO_4)_2(OH)$. Hypochlorite is bismutoferrite dispersed in quartz or chalcedony and this name should be dropped.

M. F.

Ferritungstite

D. H. RICHTER, L. E. REICHEN, AND D. M. LEMMON. *Am. Mineral.*, **42,** 83–90 (1957).

Umohoite

R. G. COLEMAN AND D. E. APPLEMAN. *Am. Mineral.*, **42,** 657–660 (1957).

M. F.

DISCREDITED MINERALS

Breislakite = (Vonsenite)

MARCELLA FEDERICO, Sulla breislakite. *Periodico mineralogia* (*Roma*) **26,** 191–210 (1957)

Breislakite, named by Brocchi in 1817, was a mineral high in iron and containing manganese, occurring in wool-like forms from Vesuvius and Capo di Bove. It was referred at various times to pyroxene, amphibole, fayalite, and ilvaite (Dana's System, 6th Ed., p. 391; App. I, p. 11; App. II, p. 19.) Analysis and *x*-ray study, including a detailed study of the structure, show that breislakite is an iron-rich member (MgO 3.22%) of the ludwigite-vonsenite series.

M.F.

Bayerite (natural) = Gibbsite

K. SASVARI AND A. ZALAI. The crystal structure and thermal decomposition of alumina and alumina hydrates as regarded from the point of view of lattice geometry. *Acta geol. acad. sci. Hung.*, **4,** 415–466 (1957)

The naturally occurring bayerite from Fenyöfö, Hungary, described by Gedeon (*Am. Mineral.*, **41,** 959 (1956)), was found by *x*-ray study to be gibbsite.

M.F.

Hydrocuprite (= Cuprite)

GEORGE SWITZER. *Am. Mineral.*, **42,** 115 (1957).

Nocerite (= Fluoborite)

CESARE BRISI AND WILHELM EITEL. *Am. Mineral.*, **42,** 288–293 (1957).

Pilbarite (= Thorogummite + Kasolite)

R. M. HONEA. *Am. Mineral.*, **42,** 908–910 (1957).

M. F.

AMERICAN MINERALOGIST

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